

ETRURIA MARL

What it is

How it formed

Why it's special

Bernard Besly - Keele University

TOPICS TO BE COVERED

What is Etruria Marl?

Typical appearance: basic chemistry and mineralogy

Where it occurs

- Geography
- Stratigraphy
- Thickness
- Relationship to Coal Measures

How was it deposited?

Palaeolatitude, palaeoclimate etc...

Depositional environment

- River systems
- Soils, weathering and early diagenesis
- Alluvial fan systems

Uses – 1 Heavy ceramics

Chemistry & mineralogy – comparison with other clays

Favourable qualities

Mineral transformation in firing (contrast with non kaolinitic clays)

Typical uses

Uses – 2 Cement

Brief history of cement making

Mineralogy of cement binders

Pozzolans

LC3 process

Planning implications

Remaining resource

Green belts and mineral protection zones

How long might it last?

What it is

WHAT IS ETRURIA MARL?



Although informally called a 'Marl' the Etruria Formation is a succession of mainly red and multicoloured mudstones

- dominated by kaolinite clay mineral
- high content of iron oxide
- generally has high silica content

Chemistry:

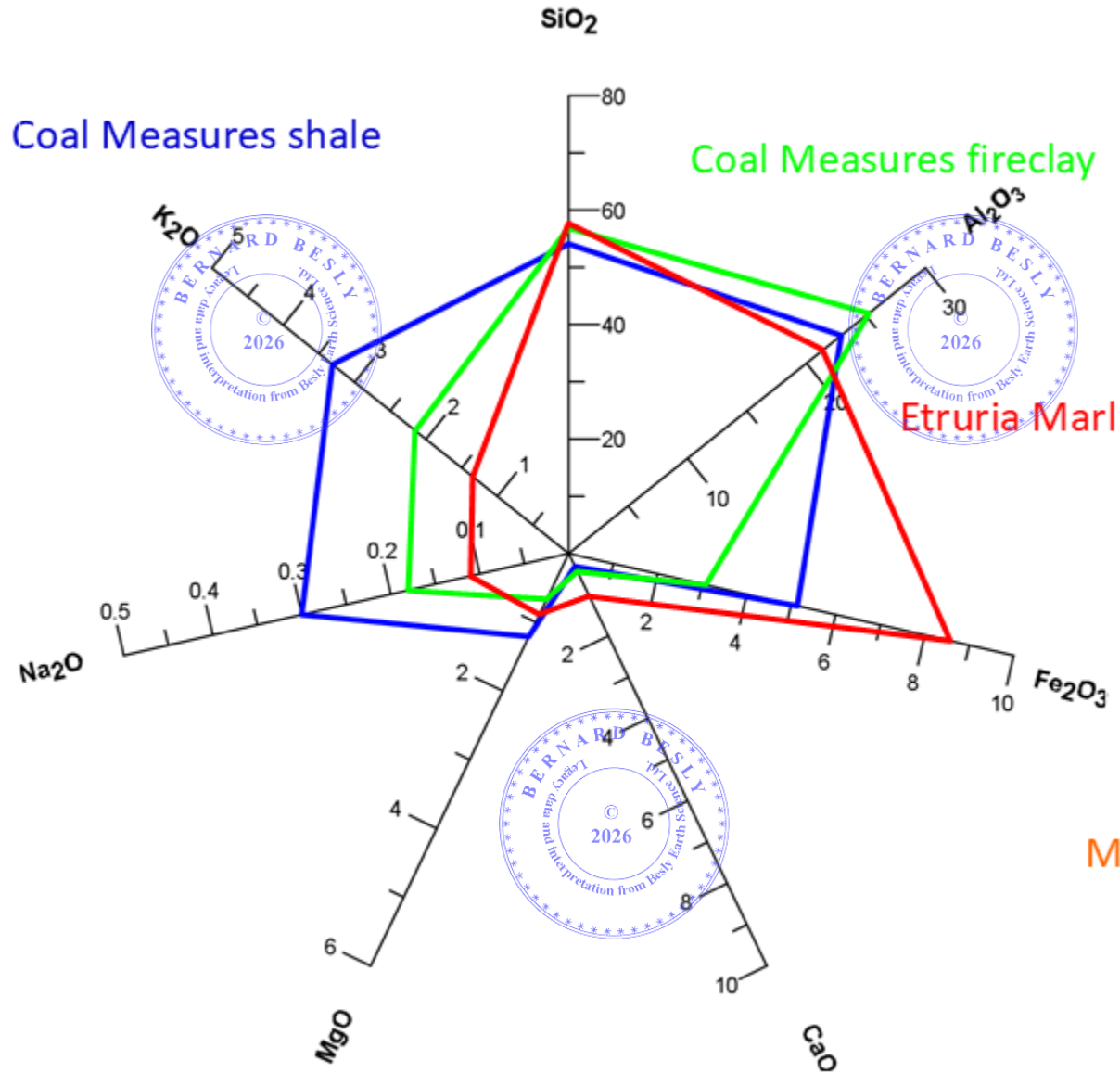
	Mean	Min	Max
SiO ₂	58.1	40.4	73.7
Al ₂ O ₃	20.9	7.0	29.0
Fe ₂ O ₃	8.5	3.4	20.0
CaO	0.9	0.1	15.8
Na ₂ O	0.2	0.0	0.6
K ₂ O	1.5	0.2	4.2

Mineralogy:

	Mean	Min	Max
Quartz	33.5	14.7	65.5
Kaolinite	38.3	12.3	67.0
Illite	15.0	2.4	38.4
Limonite'	9.7	3.6	20.6
Calcite	1.7	0.1	28.3

CLAY FINGERPRINTS

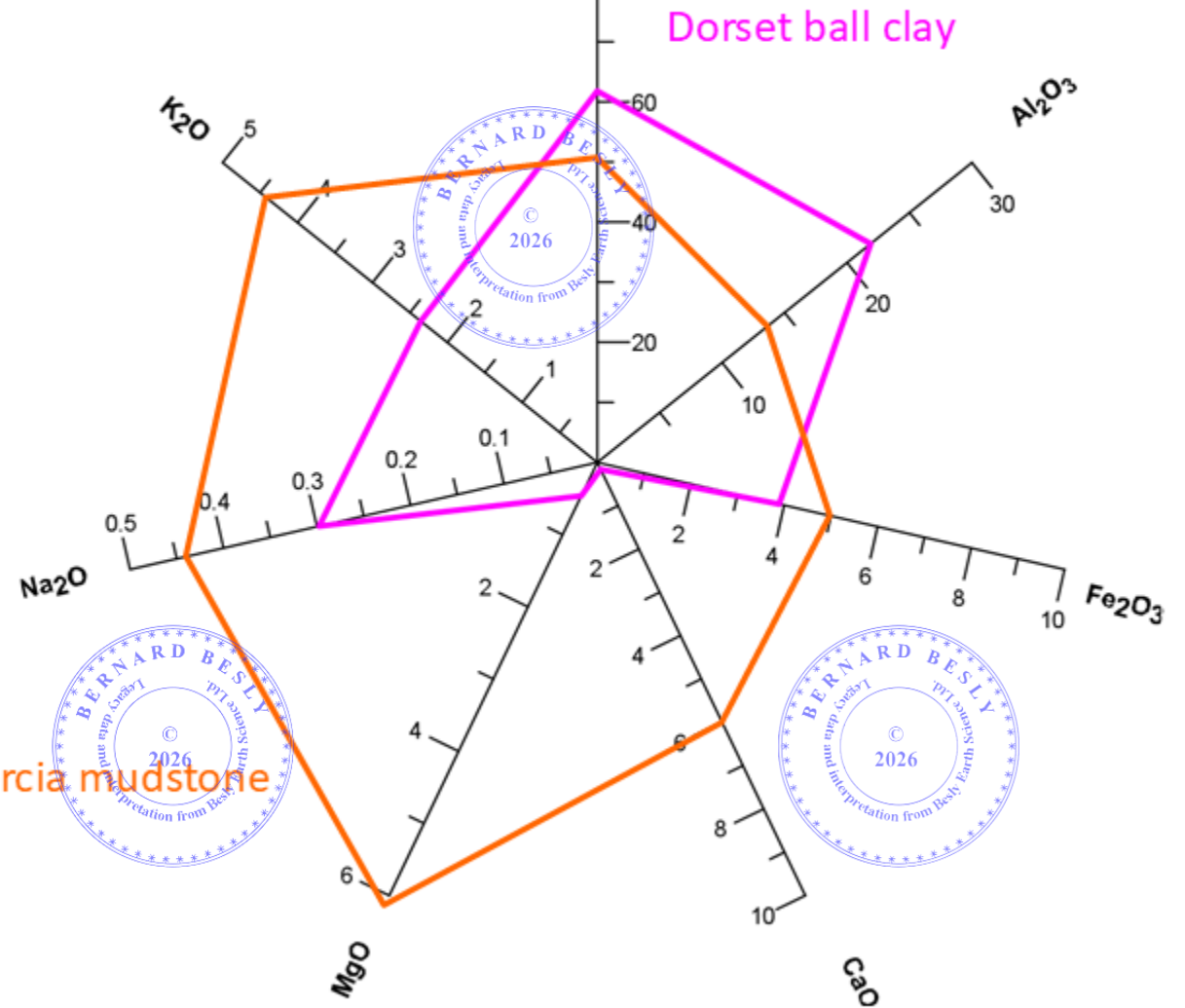
Coal Measures shale



Coal Measures fireclay

Etruria Marl

SiO₂



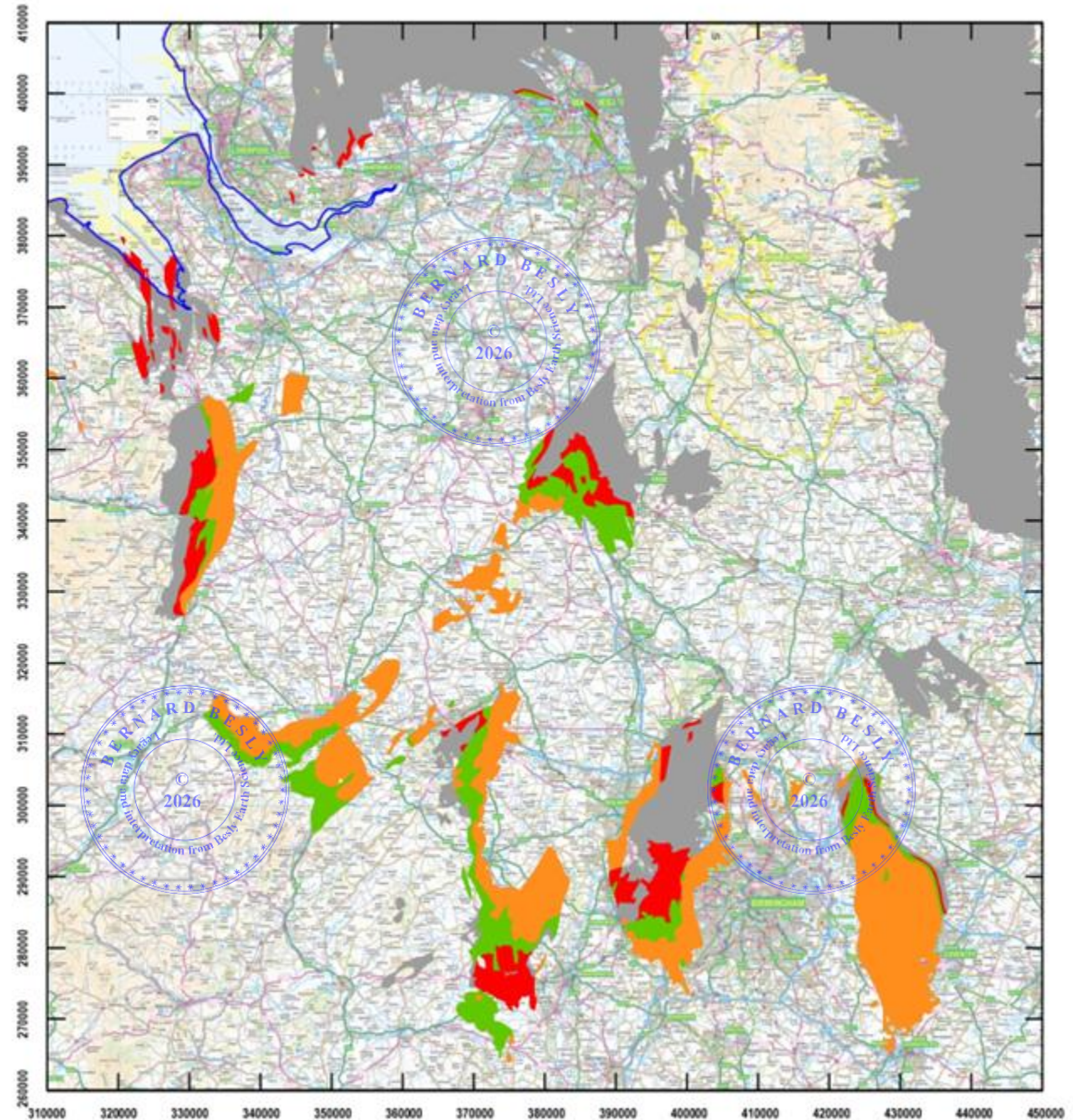
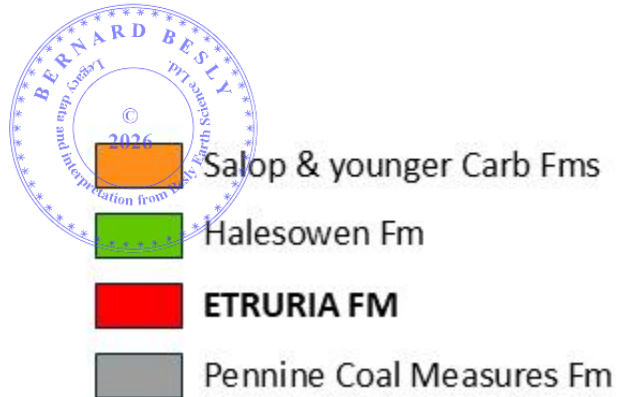
Dorset ball clay

Mercia mudstone

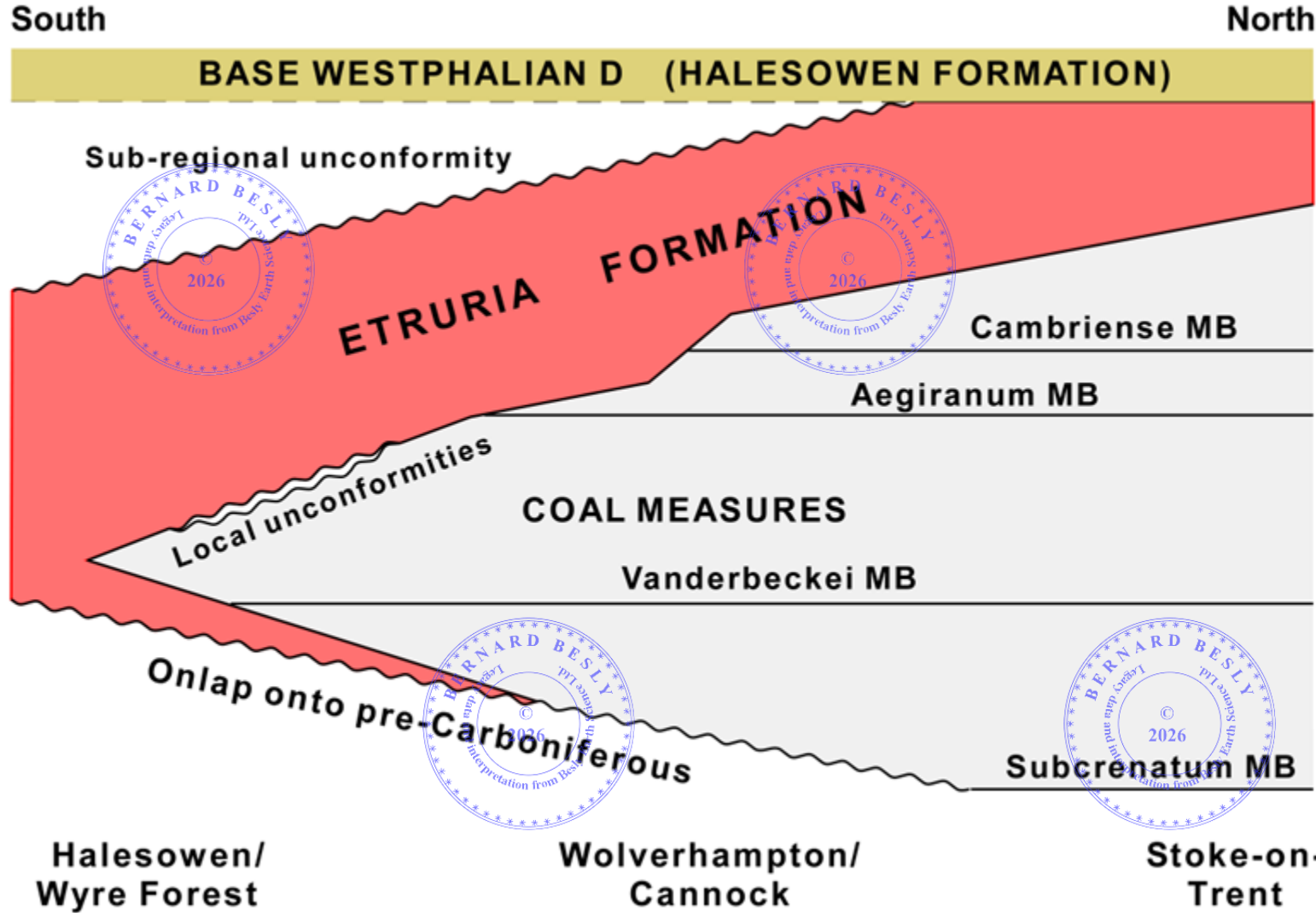
WHERE DOES IT OCCUR?

Etruria Formation lies on top of the Coal Measures in former mining areas of West Midlands and North Wales

- Not present at outcrop in Derbyshire/Nottinghamshire/Yorkshire Coalfields
- Not deposited in southern coalfields (S Wales, Bristol)



LITHOSTRATIGRAPHY



D

C

B

A

WESTPHALIAN

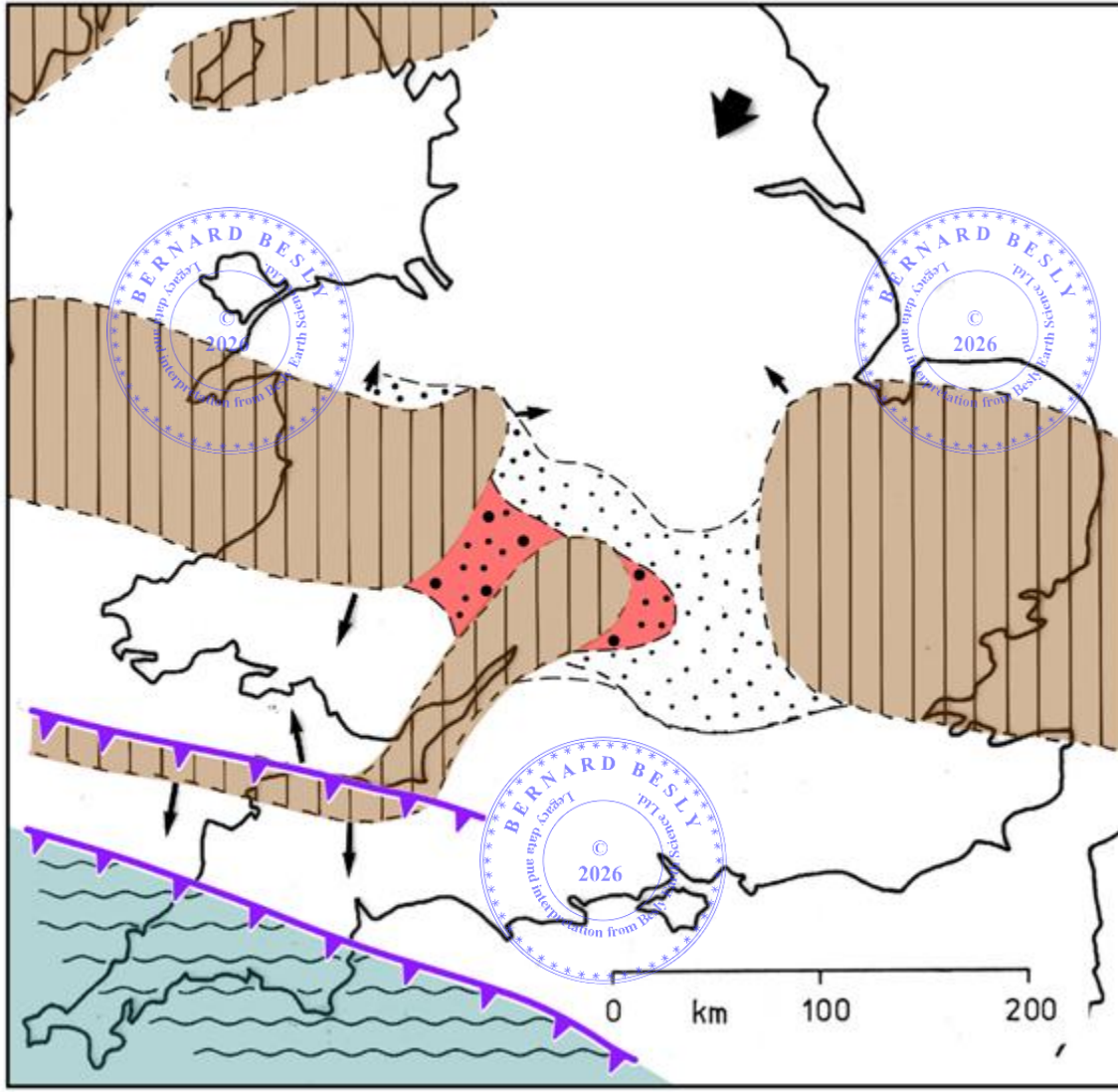
Red beds restricted to extreme south until mid Westphalian B
Thereafter spread rapidly into whole basin

Thickness
± 280m in N
± 50m in S

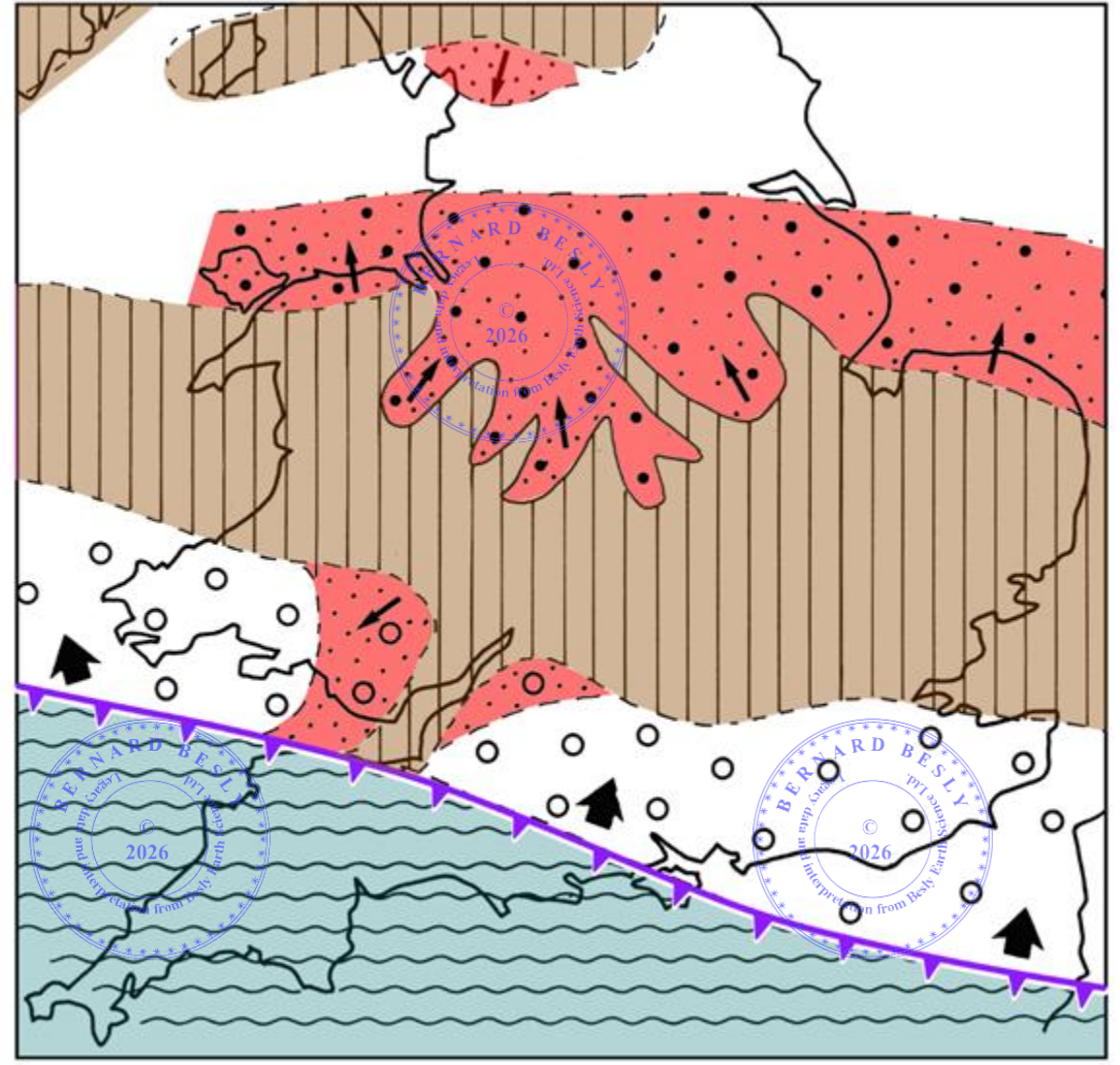
Condensed deposit



PALAEOGEOGRAPHY



Westphalian A
(Langsettian)



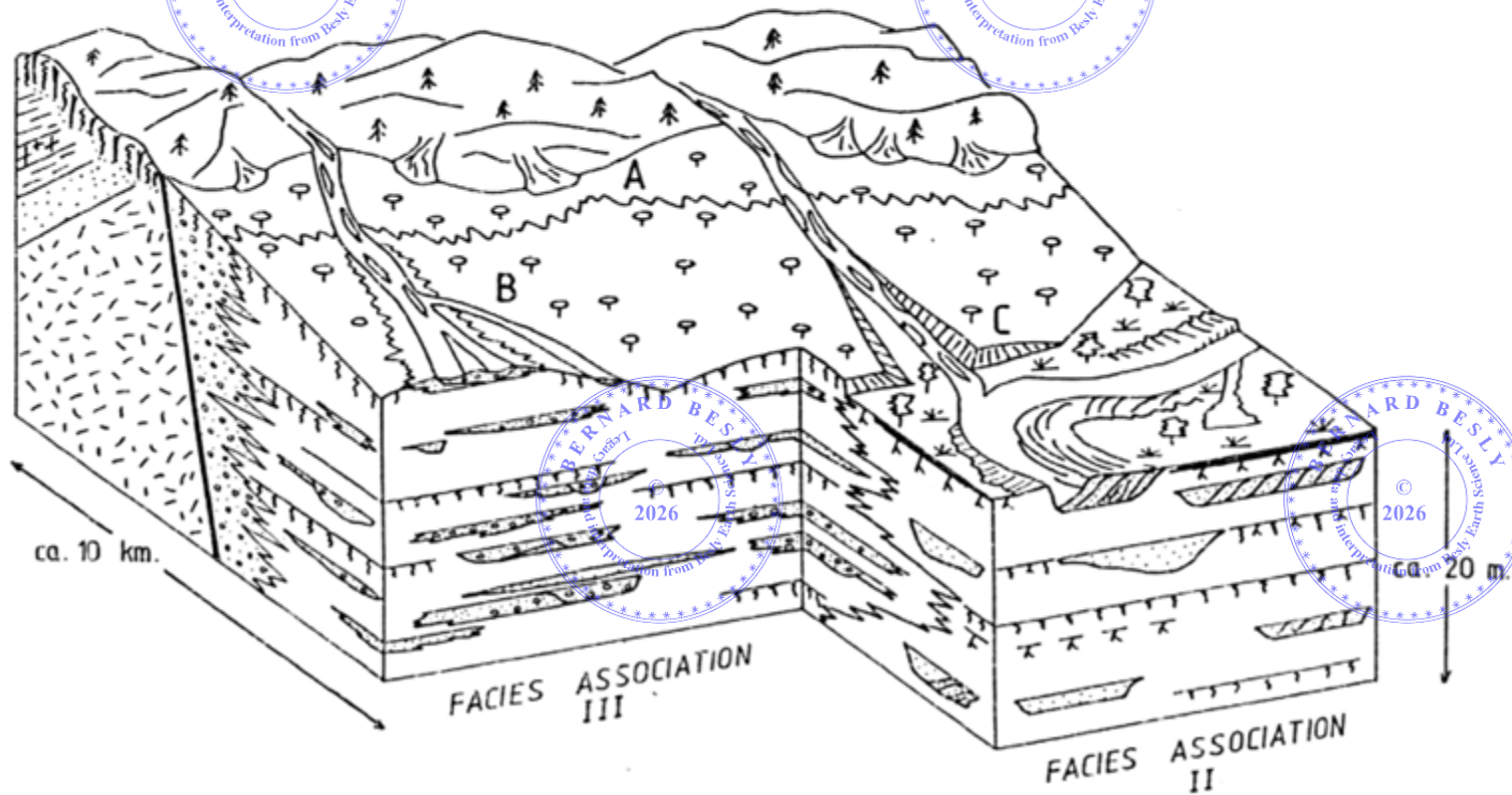
Westphalian C to early Westphalian D
(Bolsovian – Asturian)

How it formed

DEPOSITIONAL ENVIRONMENT

PALAEOSOL TYPES

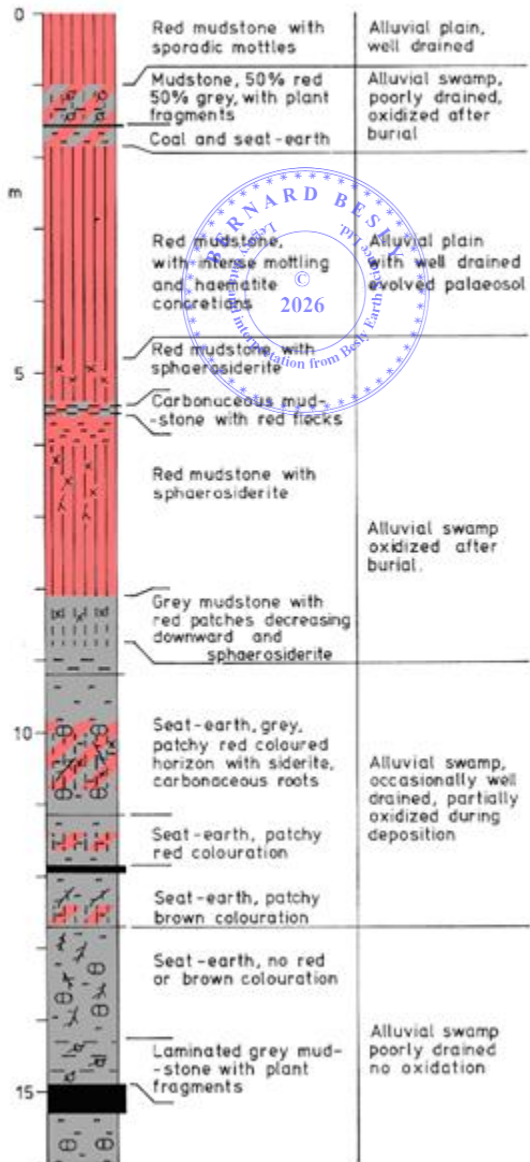
♣	Upland vegetation	— — —	1 & 2 (alluvial)
♀	Vegetation of well drained alluvium	× × ×	3 (post depositionally oxidized)
♣	Swamp vegetation	— — — —	4 (evolved - "lateritic")
		— — — —	Polyphase
		— — — —	Weathered mantle in source area



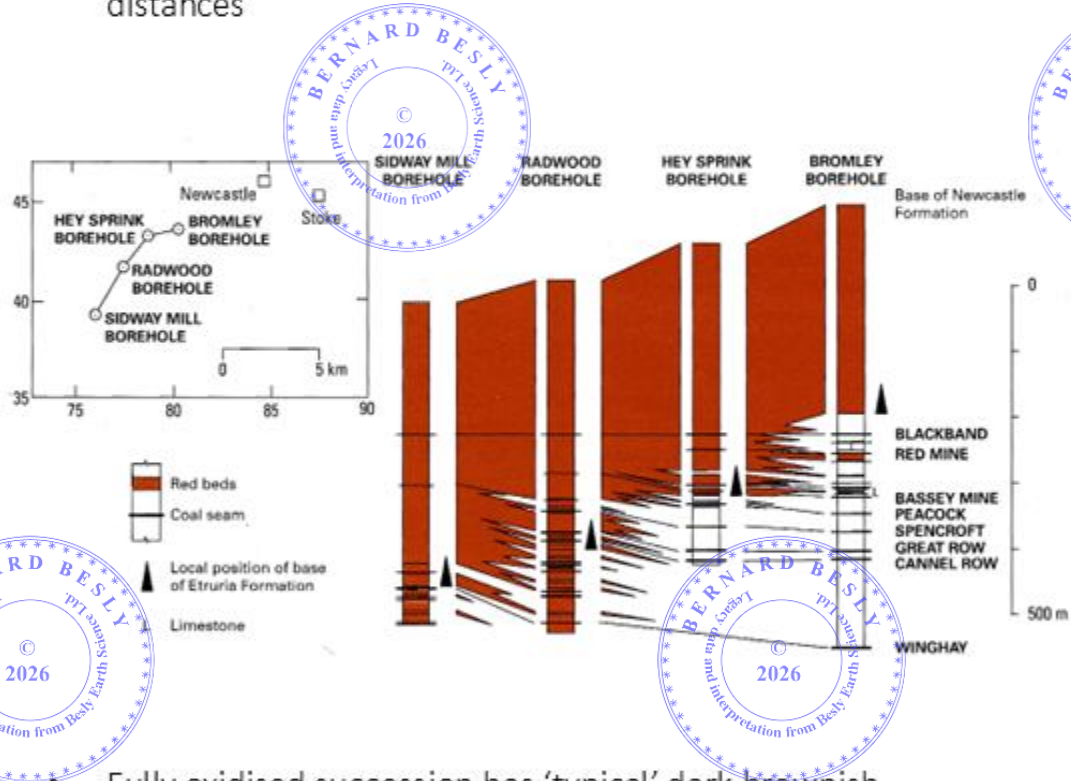
Sedimentological depositional model

- Succession deposited in tectonically active, fault-bounded basins
- Alluvial fans at margins with deposition by mudflows and high energy gravelly rivers
- Quieter river systems away from basin edges with complex channel systems depositing sandstones
- Sedimentary geometries laterally heterogeneous (i.e. the rocks do not conform to the classic sedimentary rock image of uniformly thick layers extending over large distances)
- Red bed depositing environments pass downstream into coal-bearing deposits in lower part of formation

TRANSITIONAL POORLY TO WELL-DRAINED ASSOCIATION



- Basal transition from Coal Measures through interbedded succession of increasingly oxidised soil horizons
- Significant diachronous lateral transition over short distances

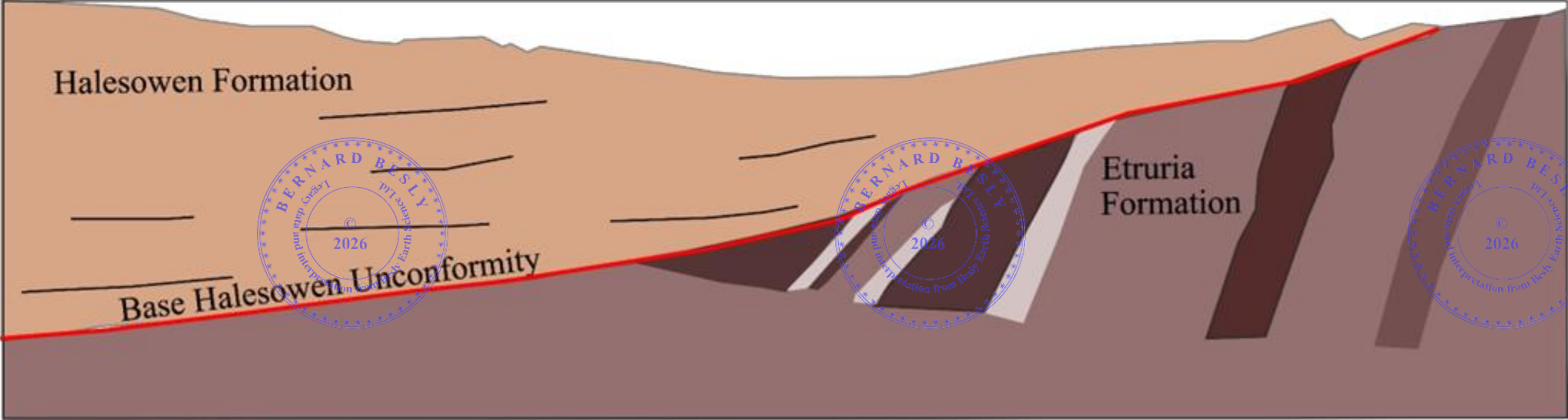


- Fully oxidised succession has 'typical' dark brownish-red Etruria Formation colour
- Transitional succession has paler grey colours; locally named with different lithostratigraphic name (e.g. "Buckley Fireclay" in North Wales)

LOCAL UNCONFORMITIES



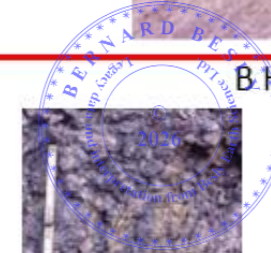
East Metres 0 10 20 30 West



WELL DRAINED ALLUVIAL PLAIN ASSOCIATION

A Horizon – strongly leached upper part

Complete soil profile



Root systems

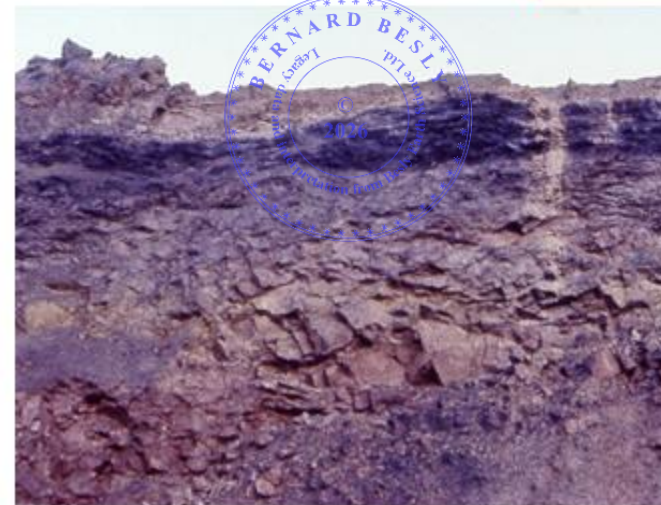


Iron nodules



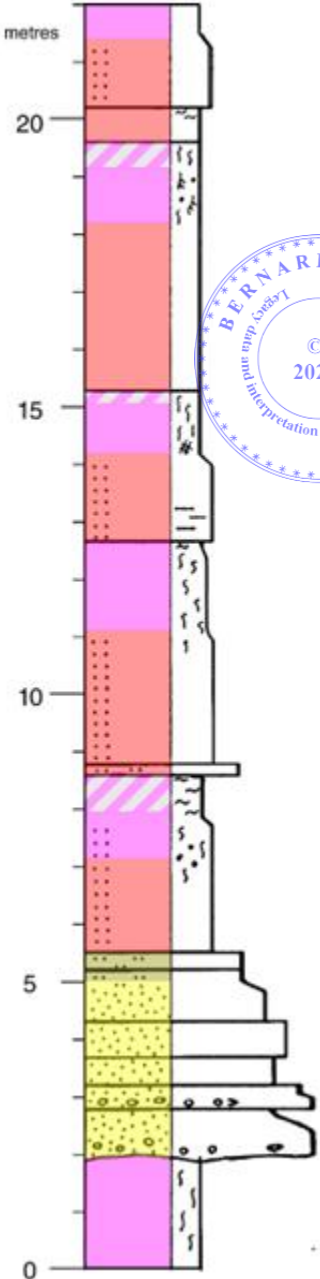
Redox textures

B Horizon – textures



Part-oxidised coal and gley soil

Evolved hiatal soil



Alluvial overbank

Hiatal soil (Ultisol / Oxisol)

Alluvial overbank

Hiatal soil (Ultisol / Oxisol)

Alluvial overbank

Hiatal soil (Ultisol / Oxisol)

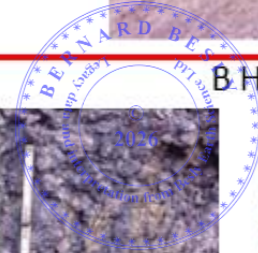
Alluvial overbank

Hiatal soil (Ultisol / Oxisol) capped by oxidised gley and peat soils

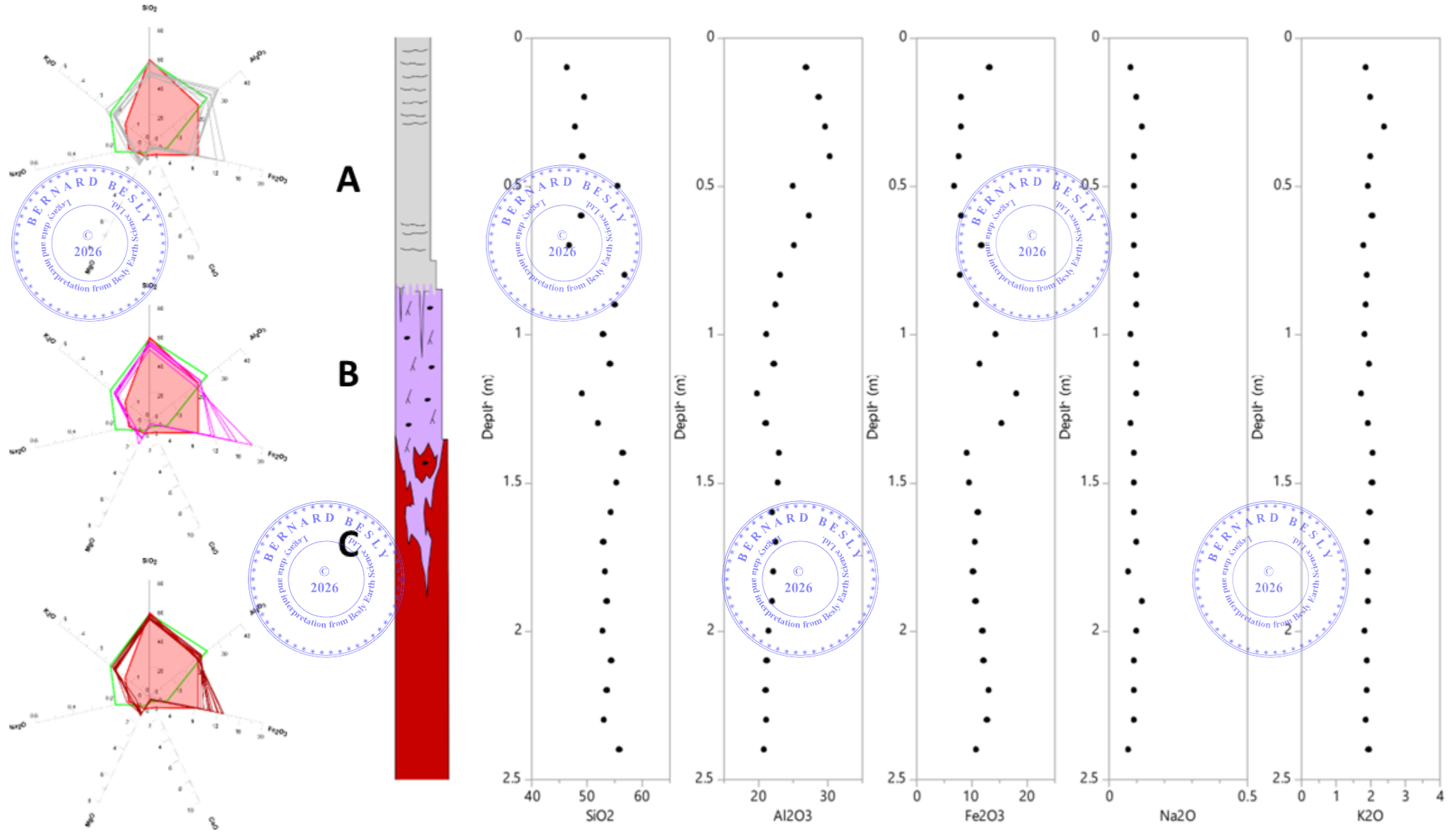
Alluvial overbank

Alluvial channel sand

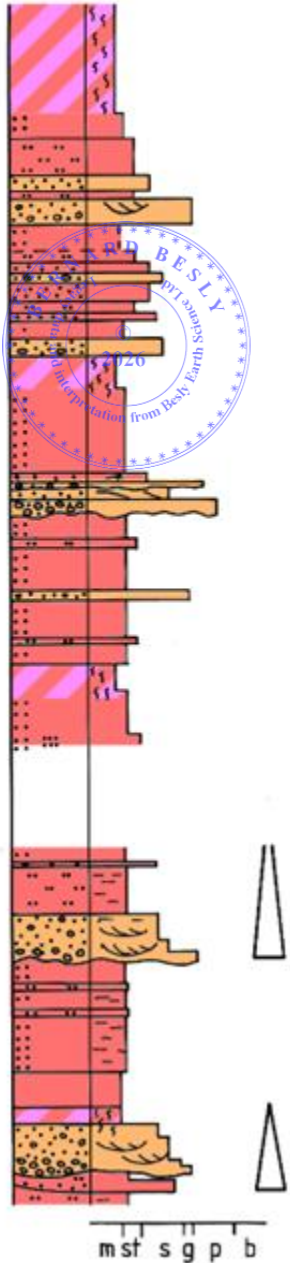
Hiatal soil (Ultisol / Oxisol)



WEATHERING PATTERN IN SOIL PROFILES

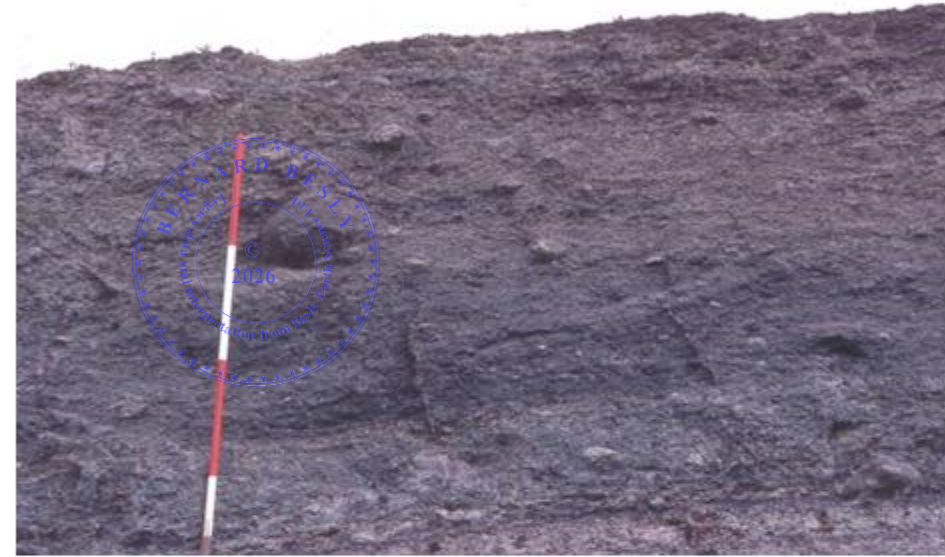


ALLUVIAL FANS



Sand and conglomerate bodies thicker and more complex

Utopia Quarry - Aug 1977

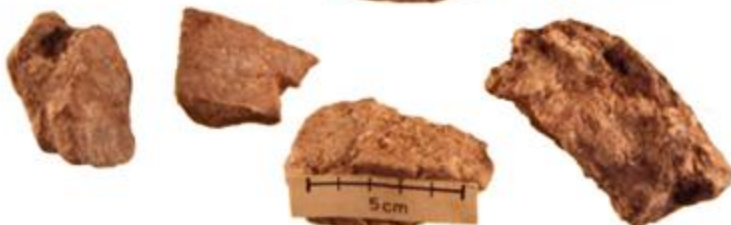


Debris flows & gravel bed braided streams

Sandstones much coarser, pebbly, often very poorly sorted



Blockleys Quarry - Sep 1978

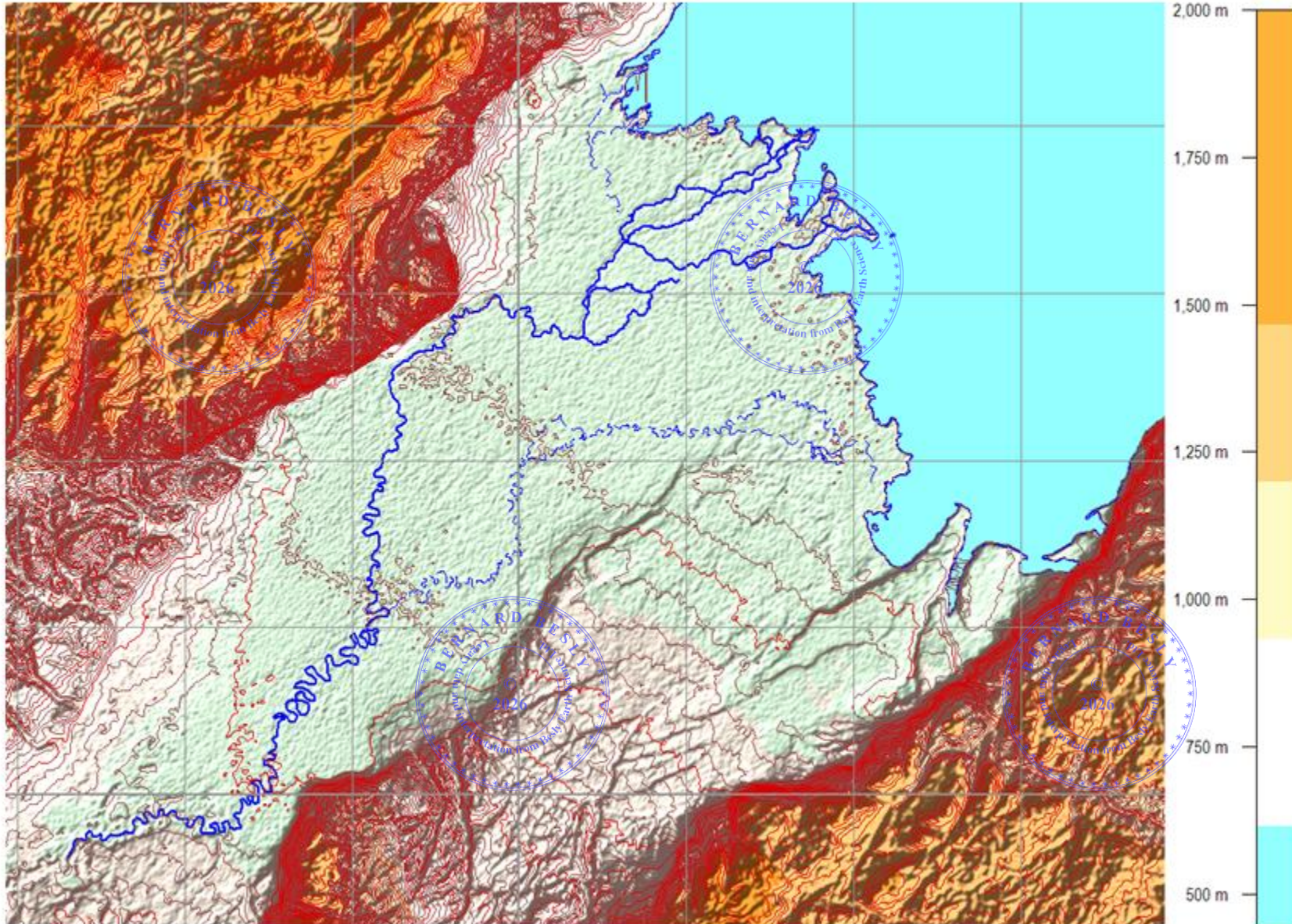


Clasts may be extremely angular, showing little distance of transport from source

Blockleys Quarry - Sep 1978



RECENT ANALOGUE – ALLUVIAL PLAINS AND LAKE

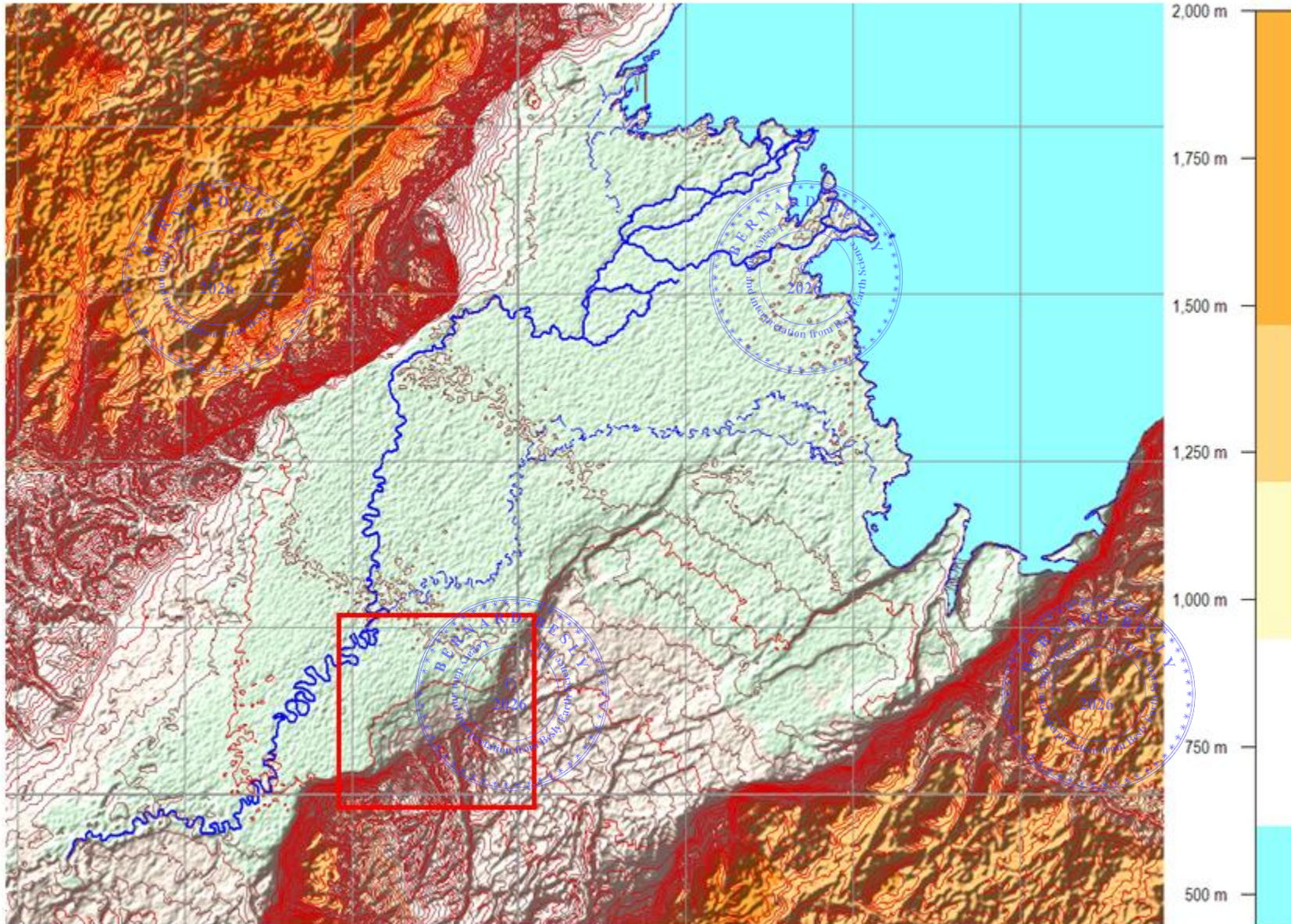


Environment in which Etruria Fm was deposited inferred to be similar to S end of Lake Albert (Uganda)

- equatorial latitude
- intense tropical weathering of source uplands
- steep faulted basin margins
- low gradient swampy river plain flowing towards
- delta building into lake

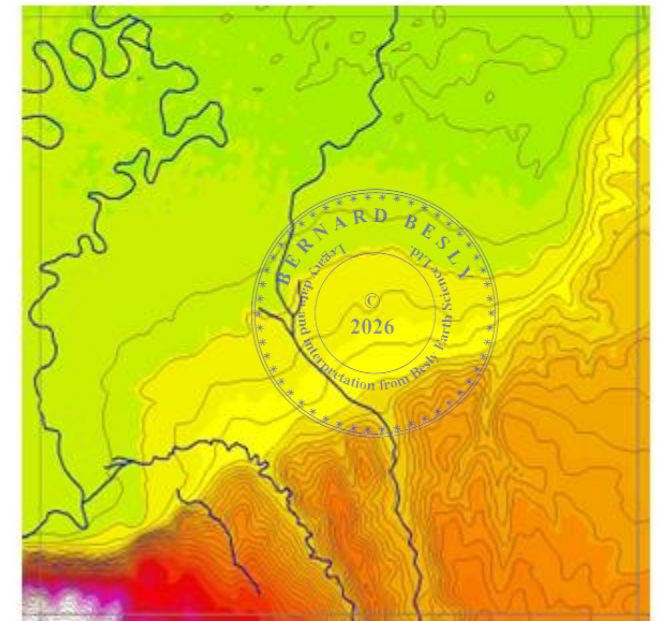


RECENT ANALOGUE – ALLUVIAL FANS



Fan-shaped cone of sediment deposited where tributary river crosses basin - bounding fault

- Gradient much steeper (1 in 70; 0.8°)
- Coarse grained immature sediment (pebbles, boulders)
- Very fast flow during flood events
- Landslides, debris flows



Kibuku Fan, Uganda Contour interval = 10m



INFLUENCE OF GEOLOGY ON QUARRY PRACTICE

Etruria Marl is a layered deposit. Layers are generally not more than $\pm 2\text{m}$ thick, often thinner. Layering exerts major control on clay composition and quality. Some layers are waste.

Geological layers are generally referred to as 'seams'.

Objective of quarrying is to produce outgoing clay that is

- reasonably homogeneous
- of predictable and consistent composition
- free of detrimental impurities

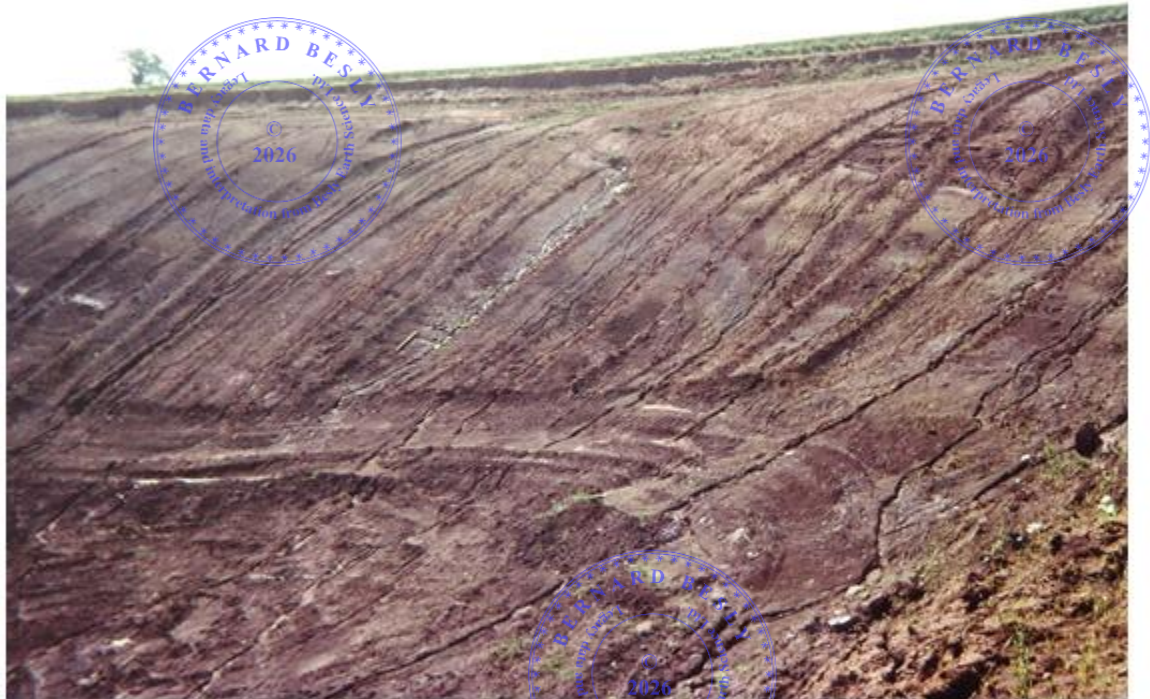
Historically this was achieved by selective manual extraction of individual seams on narrow horizontal benches followed by homogenisation in small layered stockpiles



Spoutfield Tileries— mid 1960's

HOMOGENISATION ON A LARGE SCALE

Mechanisation of extraction has produced two strategies for mixing the seams.



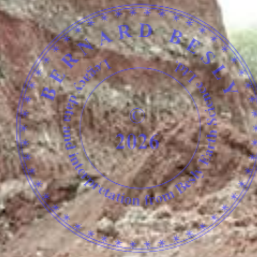
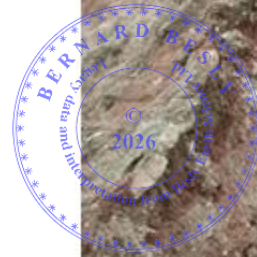
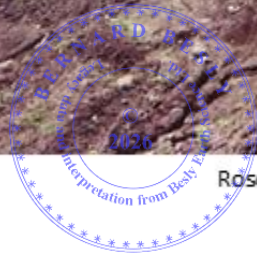
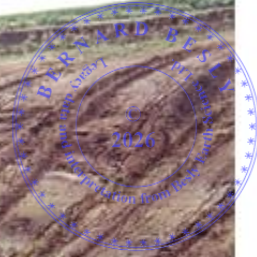
Rosemary, Cheslyn Hay- June 1977

Large layered stockpile: quarry benches follow seams; contrasting compositions layered and then mixed by taking cake slices

← Ski-slope using box scraper: seams mixed by cutting across the bedding dip

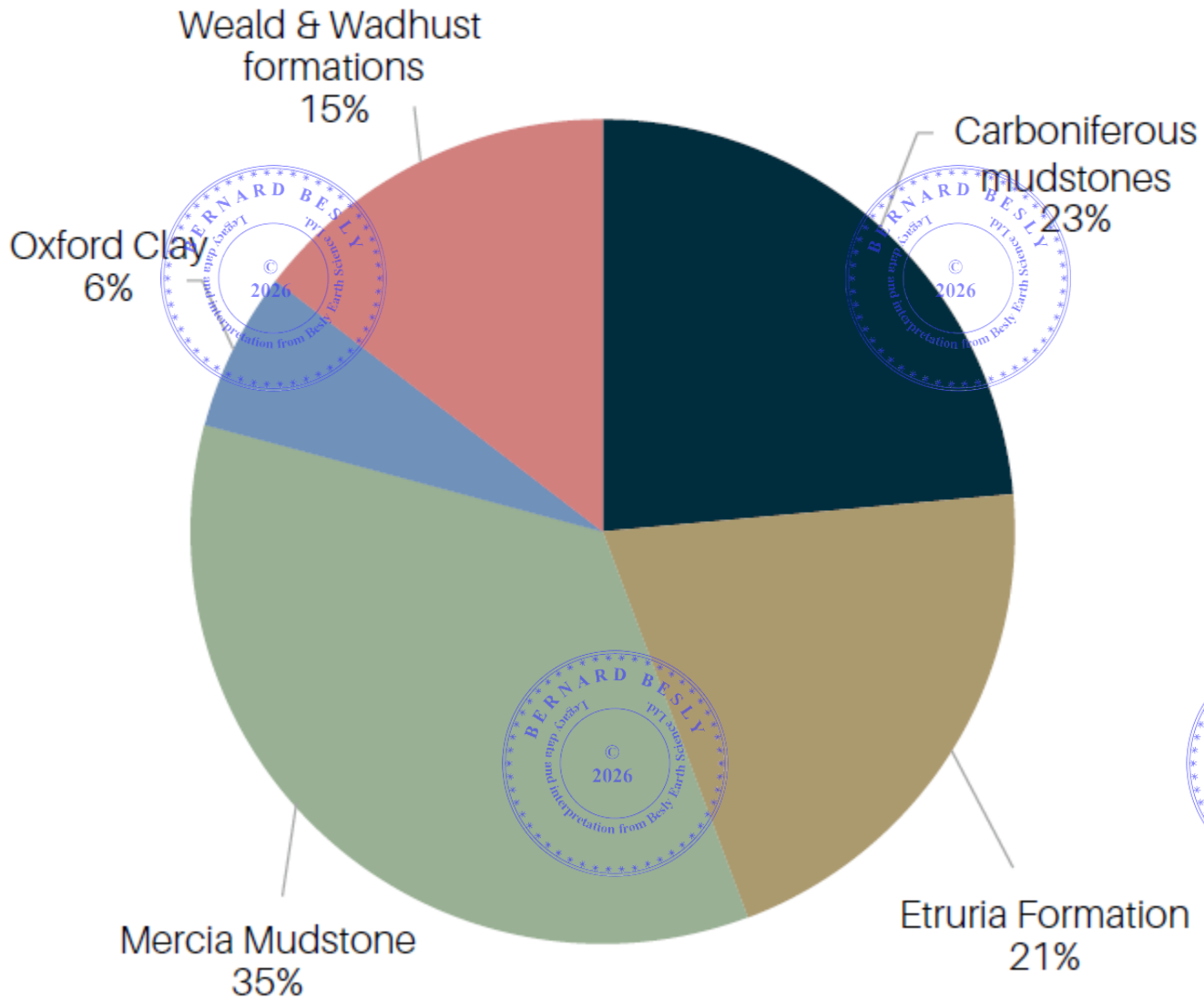


Walleys Quarry – April 2003



Why it's special – 1: ceramic properties

WHAT IS ITS CONTRIBUTION TO UK BRICK INDUSTRY?



Etruria Marl is (by a small margin) the third most important source of brick making clay in UK

- Main source of material suitable for making high strength Class A engineering bricks
- Dominant source of clay suitable for making clay roof tiles
- Regarded as “best” brick raw material for ease and consistency of manufacture and desirable inherent range of product colour

Figure 5 Great Britain: Brick production by major brick clay geological source, 2020. Source: Survey of members by the British Ceramic Confederation, 2020.

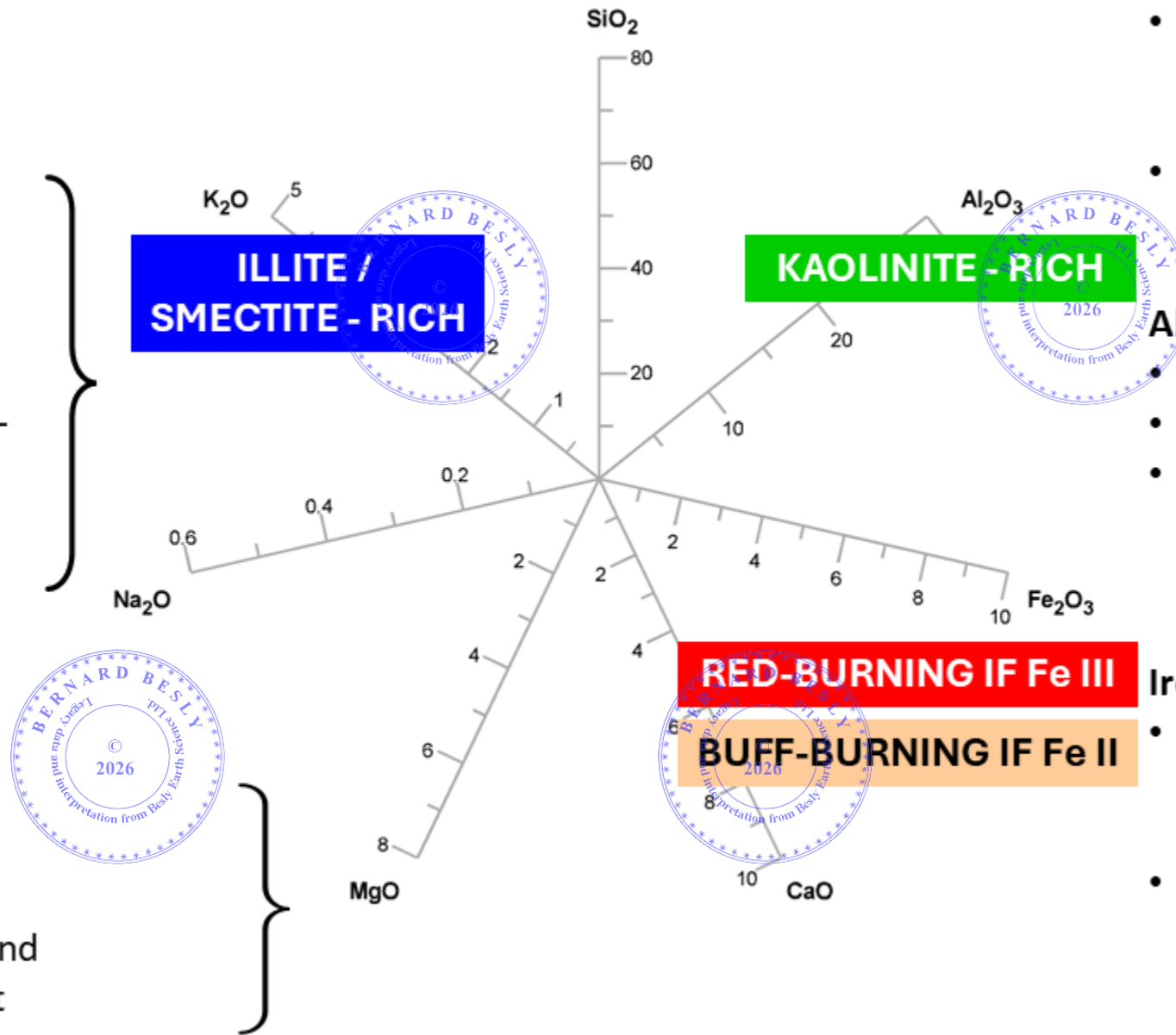
EVERYTHING YOU NEED TO KNOW ABOUT BRICK MAKING

Alkalis

- mainly in clays (and feldspars if present)
- strong fluxing agents – promote vitrification

Alkali earths

- mainly as carbonates
- fluxing agents
- affect colour
- detrimental to firing and weathering of product



Silica

- mainly quartz grains (silt and sand) – also in feldspars if present
- provides inert framework

Alumina

- mainly in clay minerals
- provide plasticity
- promotes mineral neoformation

Iron

- Associated with clays; Fe III in oxides; Fe II in carbonates
- provides colour

MINERALOGY OF SOME BRICK CLAYS

Compared with other commonly used UK brick clays, Etruria Marl has:

- Very high iron content
- Low alkali content (Na, K)
- Very low alkali earth content (Mg, Ca)

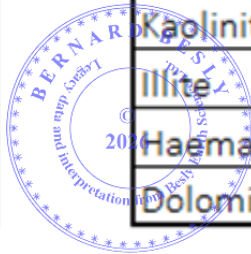


Etruria Marl

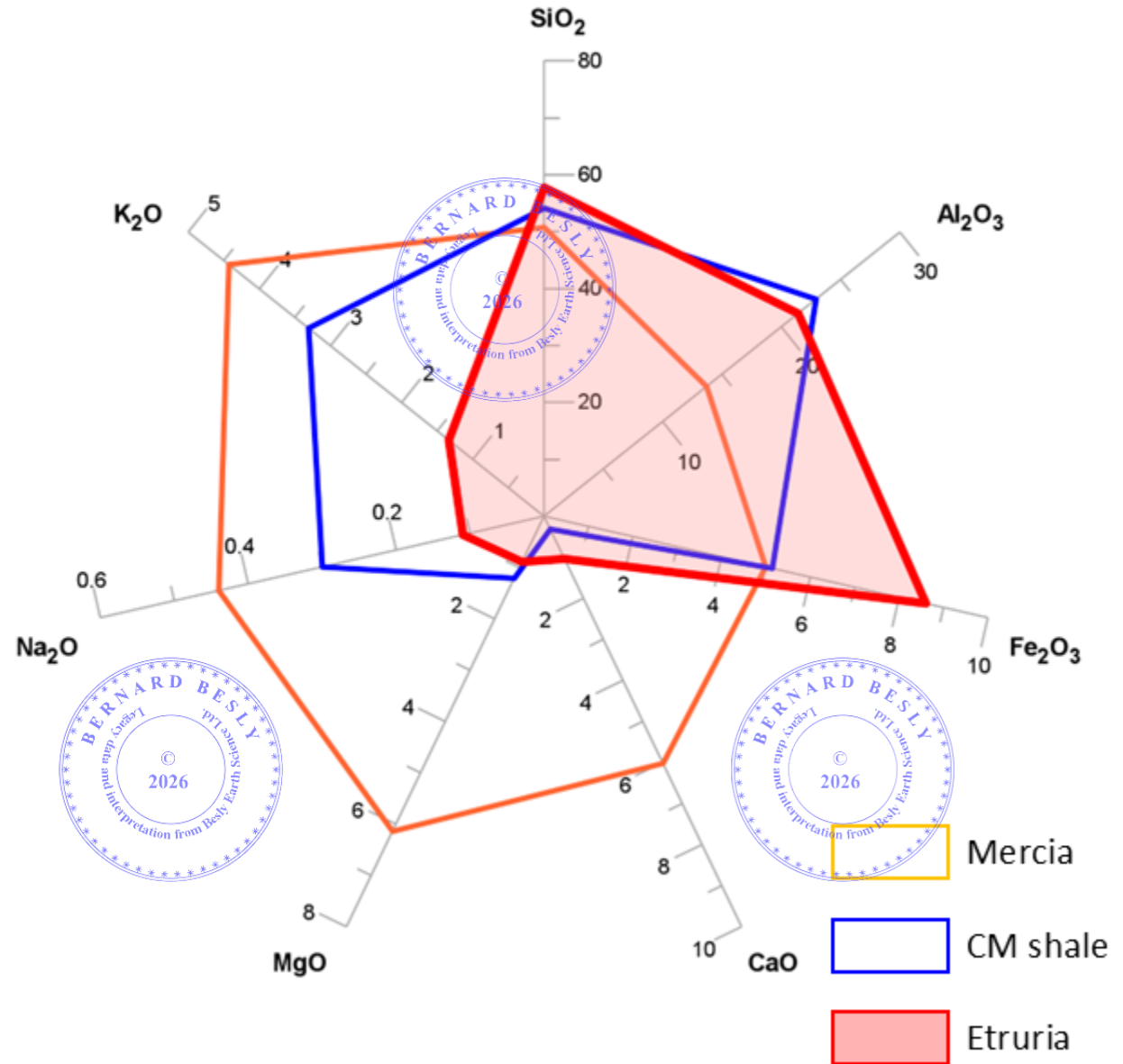
	Mean
Quartz	34.0
Kaolinite	38.0
Illite	15.0
Haematite	10.0
Calcite	2.0

Mercia Mudstone

	Mean
Quartz	50.0
Kaolinite	
Illite	32.0
Haematite	5.0
Dolomite	14.0



Etruria Marl is the only bulk clay in UK with dominant kaolinite and high iron content



CHARACTERISTICS OF FIRED ETRURIA MARL PRODUCTS

Etruria Marl produces exceptionally strong, dense and water-resistant products

- Suitable for Class A/B engineering bricks, roofing tiles, architectural ceramics, and (historically) sewer pipes

Ideal balance of clay and quartz gives a clay that can be worked reliably pre-firing

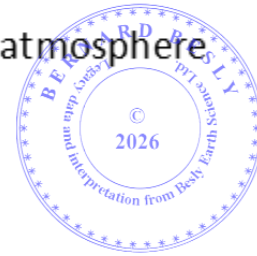
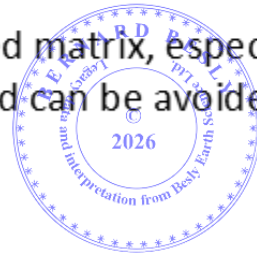
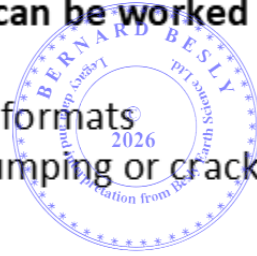
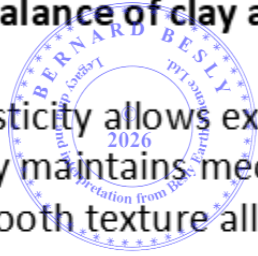
- Plasticity allows extrusion or pressing into thin formats
- Clay maintains mechanical strength without slumping or cracking
- Smooth texture allows for sharp definition

Clay composition contributes to very favourable firing regimes

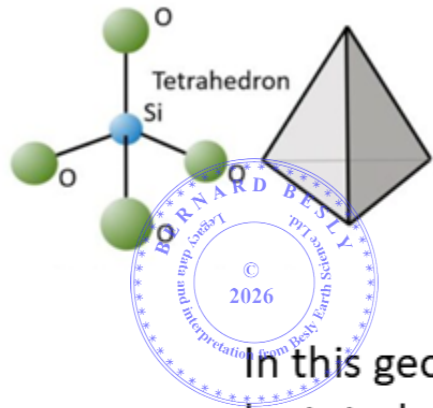
- Low carbon content allows for fast firing with low CO₂ emissions
- Little shrinkage
- Long vitrification range
- Dominance of kaolinite leads to high strength mullite-dominated fired matrix, especially when fired in reducing atmosphere
- Impurities likely to have negative impact on manufacture are rare and can be avoided in most cases

Fired products have unique properties

- Dense body with high vitrification levels gives very low porosity and permeability
- High compressive strength and weathering resistance
- Red and purple fired colours are desired aesthetic in UK

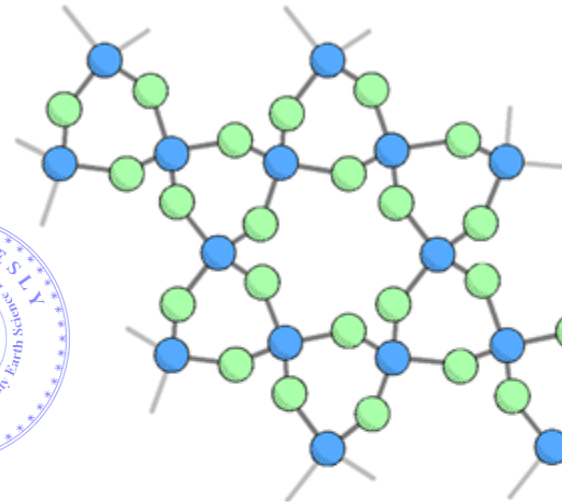


BASIC ALUMINOSILICATE STRUCTURES



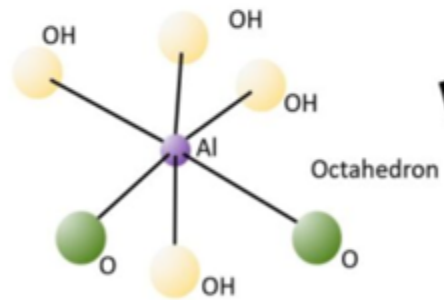
Basic building block of silicate minerals formed by simple unit of silicon atom and four oxygen atoms

In this geometry the silicon is said to be tetrahedrally coordinated



- Silicon and oxygen form macromolecule

- In simplest form this forms quartz, present in sedimentary rocks as sand and silt



Other basic building block formed by simple unit of aluminium atom, two oxygen atoms and four hydroxyl groups

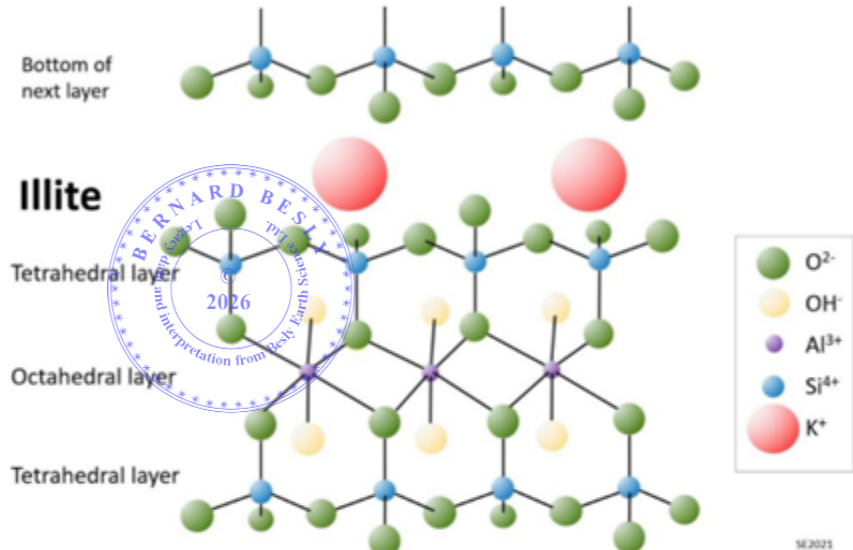
In this geometry the aluminium is said to be octahedrally coordinated

- The basic building blocks may be modified by partial replacement of silicon by aluminium: this is structure many other rock forming minerals (feldspars, pyroxenes ...)

- In these charge imbalance is corrected by presence of sodium, potassium, calcium, iron etc.....

CLAY MINERALS

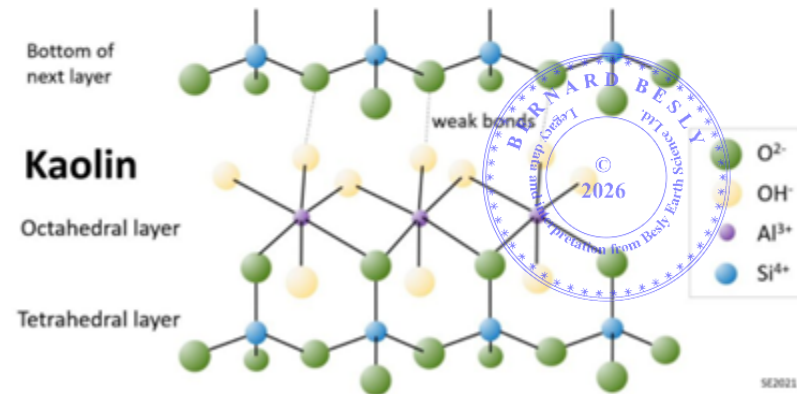
Clay minerals are sheet silicate structures constructed of layers of silicon tetrahedra and aluminium octahedra



A Representation of the Tetrahedral-Octahedral-Tetrahedral Structure of the 2:1 Clay Mineral Illite

Commonest clay mineral is illite

- Each sheet composed of two tetrahedral layers for each octahedral layer
- Charge balance between sheets provided by potassium
- Hydroxyl groups all within the sheet structure
- Resulting clay mineral type called 2:1 clay: this is typical of almost all clay minerals



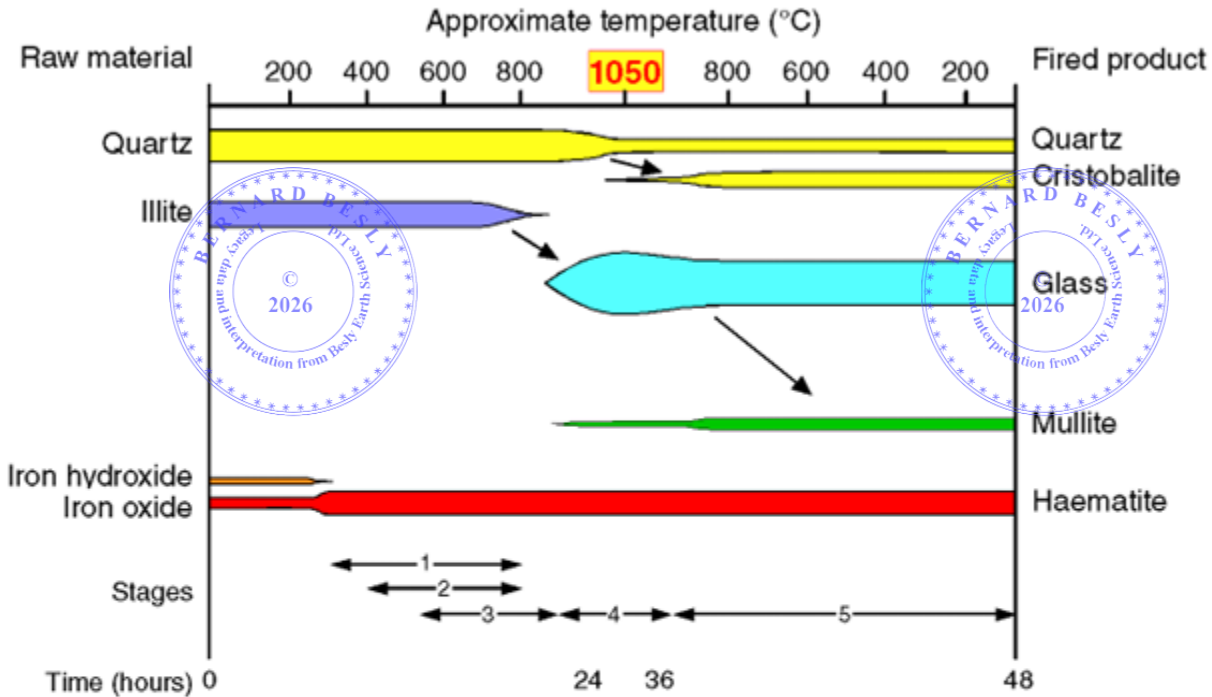
A Representation of the Tetrahedral-Octahedral Layer Structure of the 1:1 Clay Mineral Kaolin. The layers are held together with weak van der Waals bonds.

Kaolinite is the only common exception to 2:1 clay structure

- Each sheet composed of one tetrahedral layer for each octahedral layer (i.e. 1:1 clay)
- No charge imbalance
- Layers held together by weak electrostatic bonds
- Hydroxyl groups form boundaries of sheet structure

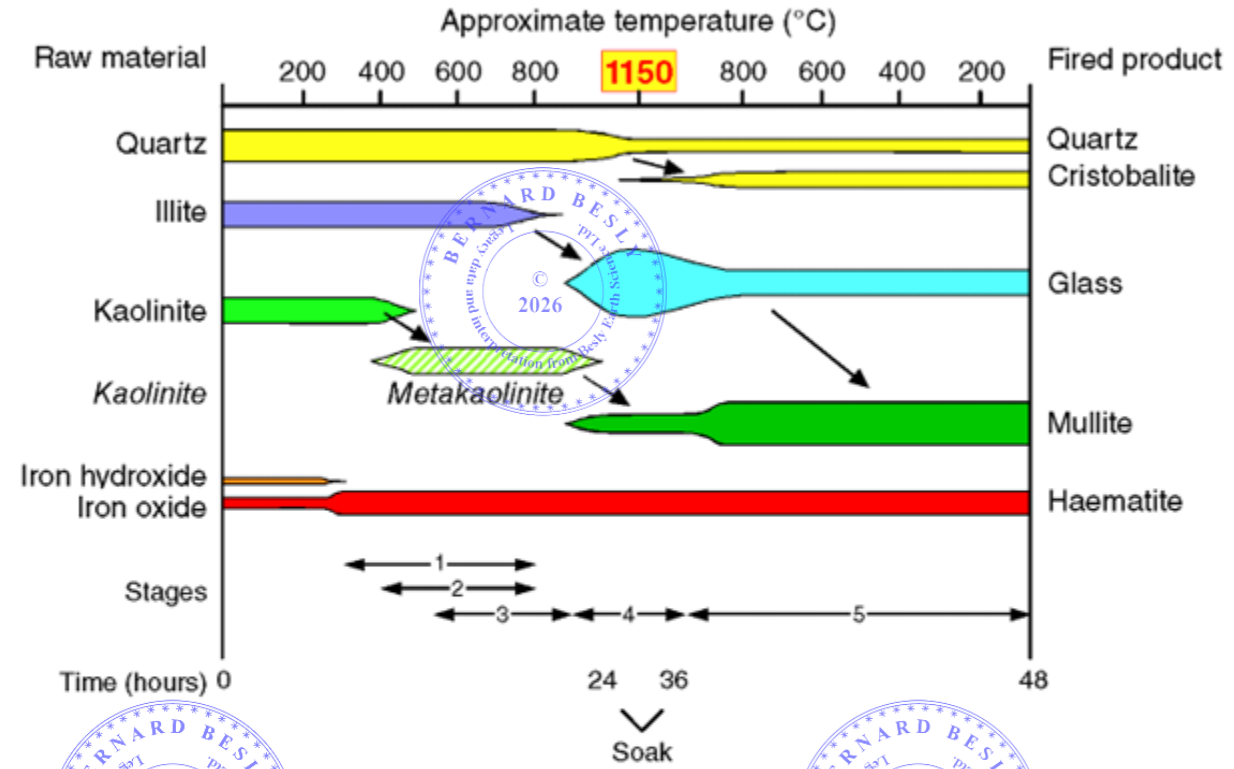
FIRING REGIME AND CLAY TRANSFORMATION REACTIONS

Illite-dominated clay



- 2:1 clay minerals melt around $1000^{\circ} - 1100^{\circ} \text{C}$
- Carbonate if present acts as flux narrowing vitrification range and lowering firing temperature
- Minor mullite production from melt
- Ceramic framework mainly held together by glass phase

Kaolinite-dominated clay

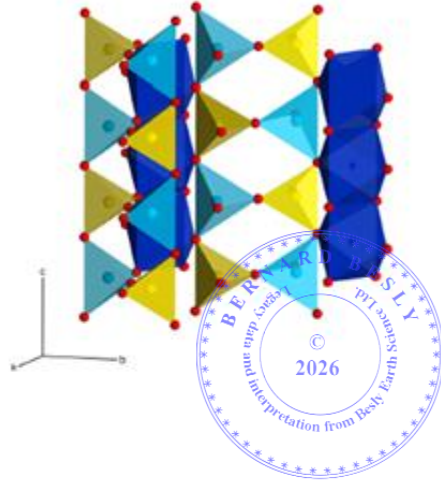


- Kaolinite melts above firing temperature ($\pm 1770^{\circ} \text{C}$)
- Kaolinite dehydration in interval $500 - 850^{\circ} \text{C}$ creates metakaolin which evolves into mullite in interval $900^{\circ} - 1100^{\circ} \text{C}$
- Minor illite acts as flux: partial melting above 1000°
- Ceramic framework held together by glass phase and mullite

Firing stages: 1) dehydration of clays & iron hydroxides; 2) burn-off of C, loss of CO_2 from carbonates; 3) solid-state mineral reactions; 4) melt production; 5) reactions on cooling
Simplified from Dunham 1992

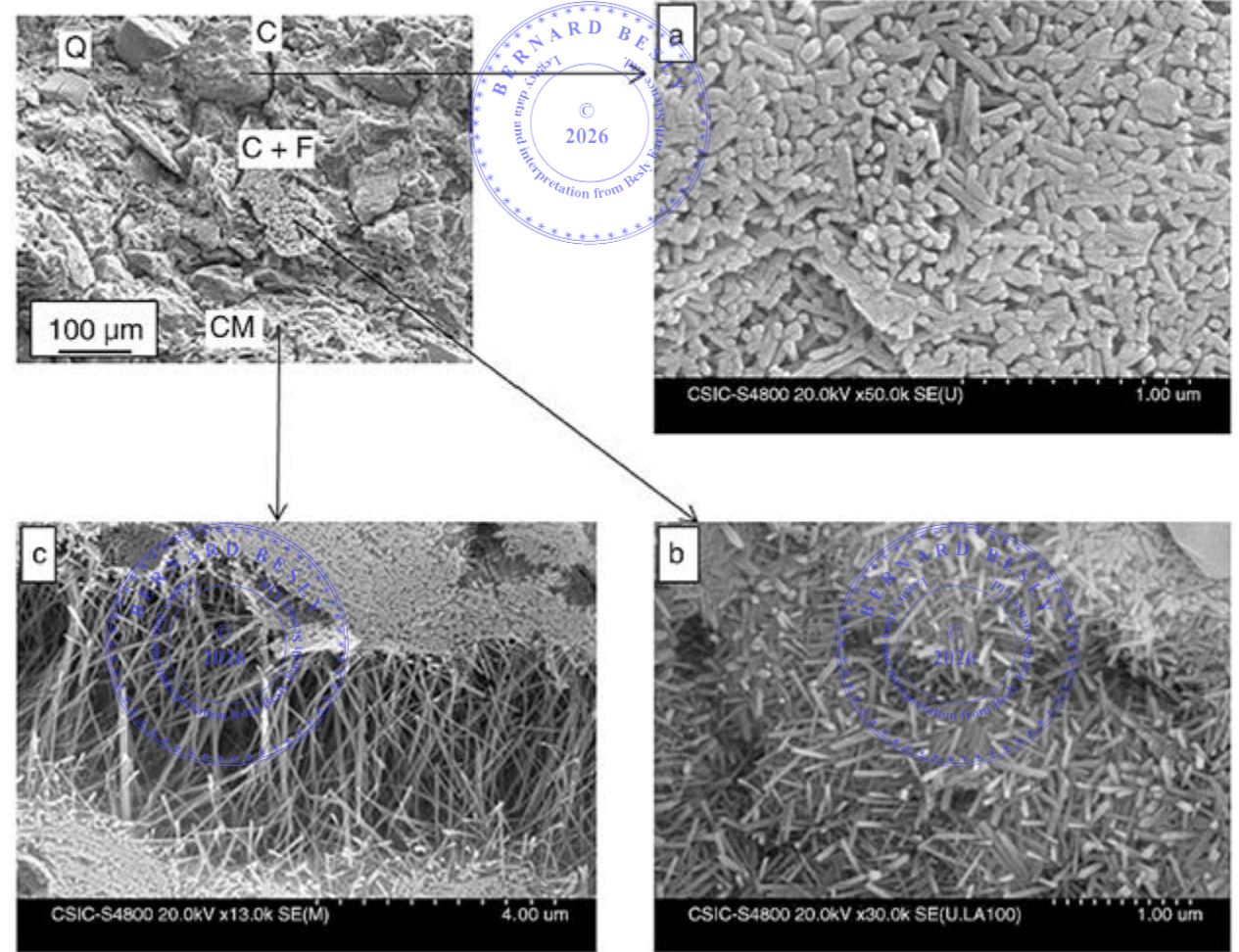
MULLITE

Disordered sillimanite



Two mullite crystal forms

- Blocky crystals formed by solid state reaction from metakaolin
- Acicular and fibrous crystals produced from melt phase if fluxing agent present
- Fluxing occurs in Etruria firing if Fe₃ is reduced to Fe₂ during peak temperature soak



Stoneware body at intermediate stage in firing (1000°C) – Romero & Pérez 2015

Why it's special – 2: pozzolanic properties

A SHORT HISTORY OF CEMENT

Type	Date	Raw material(s)	Calcination	Setting	UW	Setting mechanism	Comments
Lime mortar	BCE	Limestone	$\pm 900^{\circ}\text{C}$	Slow	N	Regrowth of CaCO_3 from CaOH_2	Self-healing
Hydraulic lime	1756 (Smeaton)	Arg limestone	$\pm 900^{\circ}\text{C}$	12 hr / 90 days	Y	a/a → CASH / CSH gels	
"Roman cement"	1796 (Parker)	"Cementstone"	$\pm 1000^{\circ}\text{C}$ (?)	Almost instantaneous	Y	CSH gel	
Portland Cement	1824 / 1840 (Aspdin)	Limestone / shale / gypsum → clinker	$\pm 1400^{\circ}\text{C}$	1 hr / 28 days *	Y	CSH gel	Setting time moderated by gypsum addition

Pozzolanic cement	1st Century AD	Limestone / natural pozzolans	$\pm 900^{\circ}\text{C}$	As for hydraulic lime	Y	Regrowth of CaCO_3 from CaOH_2 Slow strengthening through CASH gels	CASH gels mop up excess Ca Final strength after 1 year
-------------------	----------------	-------------------------------	---------------------------	-----------------------	---	------------------------------------------------------------------------------------------	-----------------------------------------------------------

A LONGER HISTORY OF CEMENT - 1: LIME-BASED CEMENTS

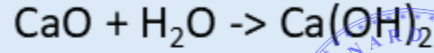
Lime mortar

Limestone calcined
at **900 - 1000°C**



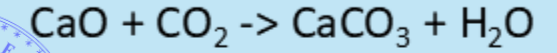
Aggregate / construction materials bonded by growth of new CaCO_3 crystals

Add water to form
slaked lime



Add sand and water

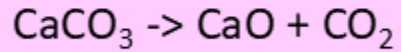
Set and cure with
atmospheric CO_2



- Very slow initial set (**weeks**); final cure months to years
- Low strength
- Flexible, self-repairing
- Does not set under water

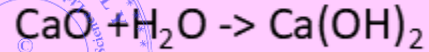
Hydraulic lime

Argillaceous limestone
calcined at **900 - 1000°C**



“hydraulic phases”

Slaked lime



Hydraulic phases
unaffected

Add sand and water

– initial set

Inert aggregate



Cure with atmospheric CO_2



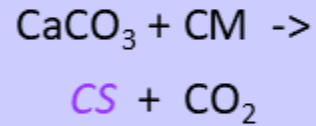
Aggregate / construction materials bonded by growth of C-S-H gels from hydraulic phases + new CaCO_3 crystals from CaOH_2

- Initial set in 4 – 12 hours; final cure 90 days
- High strength, brittle
- Sets under water

A LONGER HISTORY OF CEMENT - 2: CLINKER-BASED CEMENT

Ordinary Portland Cement (OPC)

Argillaceous limestone
and/or limestone + clay
mixture calcined at
±1400°C



Glassy clinker ground to powder;
gypsum added to moderate setting rate

Add sand and water – immediate set +
rapid cure



Aggregate / construction materials bonded by growth of C-S-H
gels from hydraulic phases only

- Initial set in 30 mins – 2 hours; final cure 28 days
- Very high strength, brittle
- Sets under water

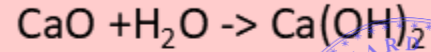
ROMAN CONCRETE – ROLE OF POZZOLANS

Argillaceous limestone
calcined at **900 - 1000°C**

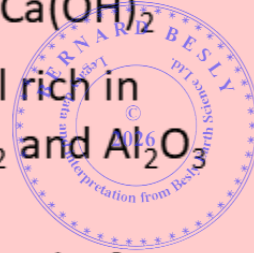


Aggregate / construction materials bonded by growth of C-A-S-H
gels from hydraulic phases + new CaCO_3 crystals from CaOH_2

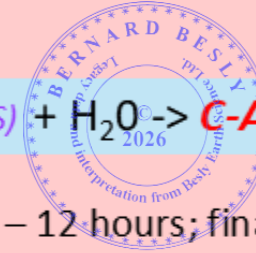
Slaked lime: add
pozzolan



Any material rich in
amorphous SiO_2 and Al_2O_3



Add sand and water
– initial set



Cure with atmospheric CO_2

- Initial set in 4 – 12 hours; final cure 90 days
- High strength, brittle
- Sets under water

C-A-S-H gels are formed if reactive aluminous phases are present in the powdered raw cement - **pozzolans**

- formulation originally developed by Romans using acid-intermediate tuffs from Pozzuoli (hence generic name)
- crushed brick
- power station fly ash
- finely ground blast furnace slag

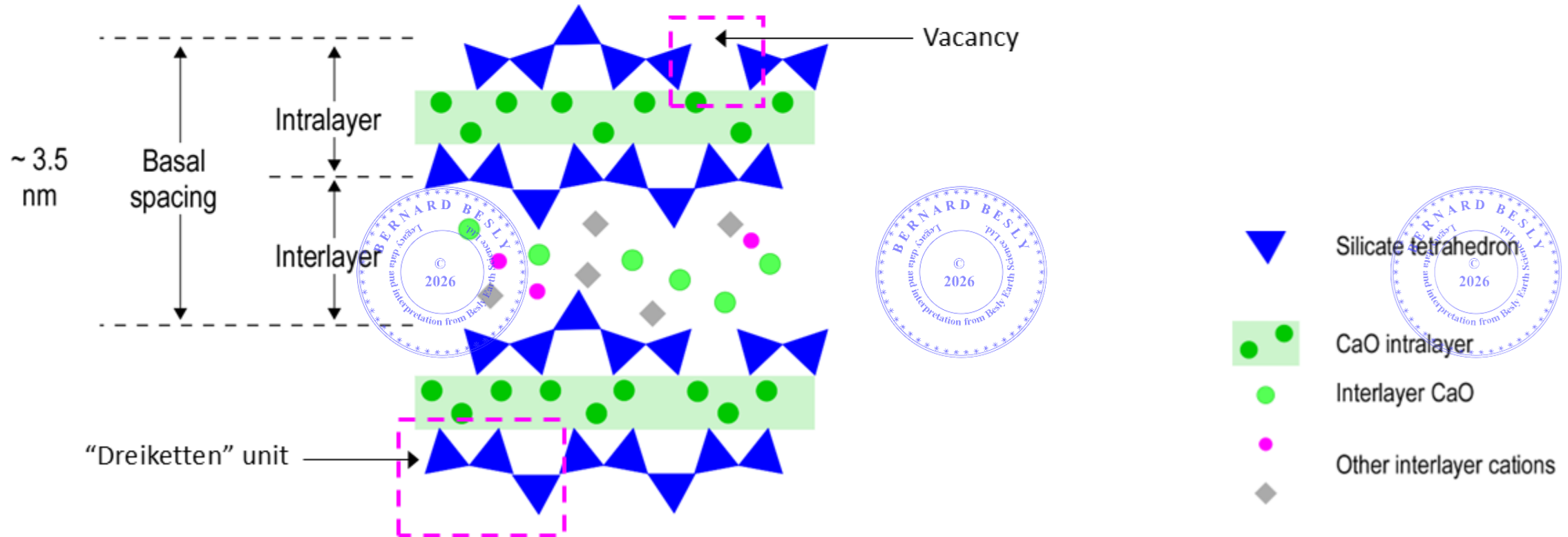


CALCIUM SILICATE HYDRATE [C-S-H]

Portland Cement clinker is a glass comprising unstable, amorphous non-stoichiometric phases:

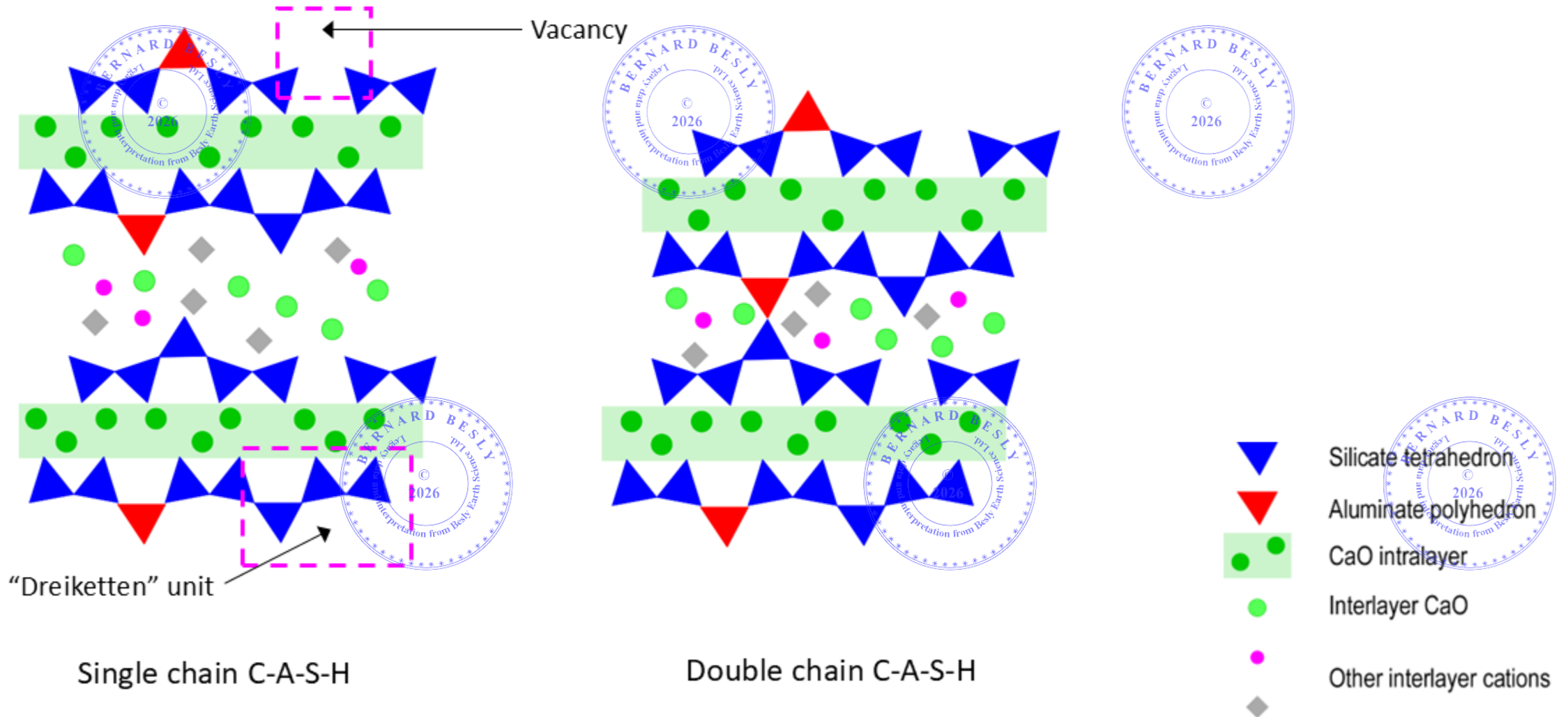
- Tricalcium silicate (C_3S – “alite”)
- Dicalcium silicate (C_2S – “belite”)
- Tricalcium aluminate (C_3A)

When finely ground these are highly reactive to water, forming C-S-H gels which solidify rapidly



CALCIUM ALUMINIUM SILICATE HYDRATE [C-A-S-H]

Gels having a slightly different composition are formed if reactive aluminous phases (**pozzolans**) are present in the powdered raw cement



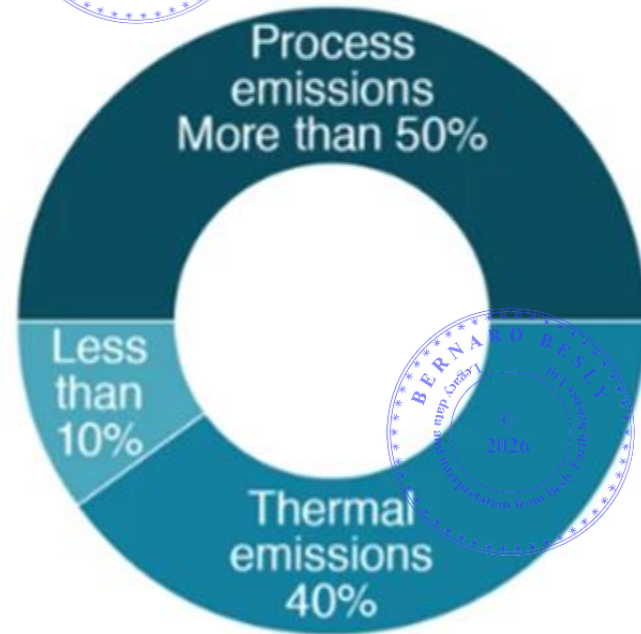
THE DECARBONISATION CHALLENGE

Cement production is a major CO₂ emitter:

- Calcination at 1400°C is fuel intensive
- Breakdown of limestone emits CO₂

In 2016 world cement production generated c. 2.2 billion tonnes of CO₂ ≈ 8% of global emissions

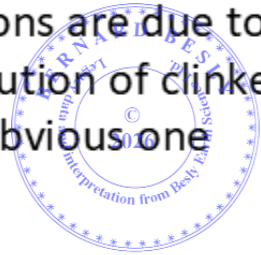
- Quarrying & transport
- Grinding & preparation of raw materials
- Cooling, grinding, mixing



Clinker production

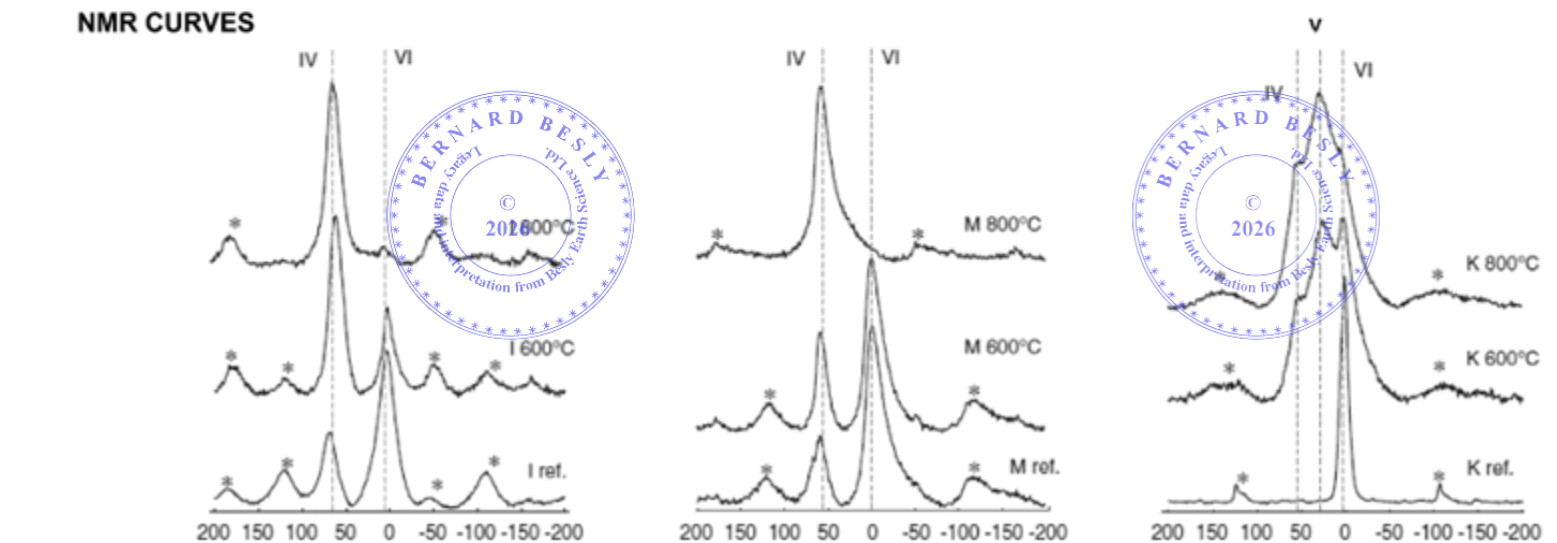
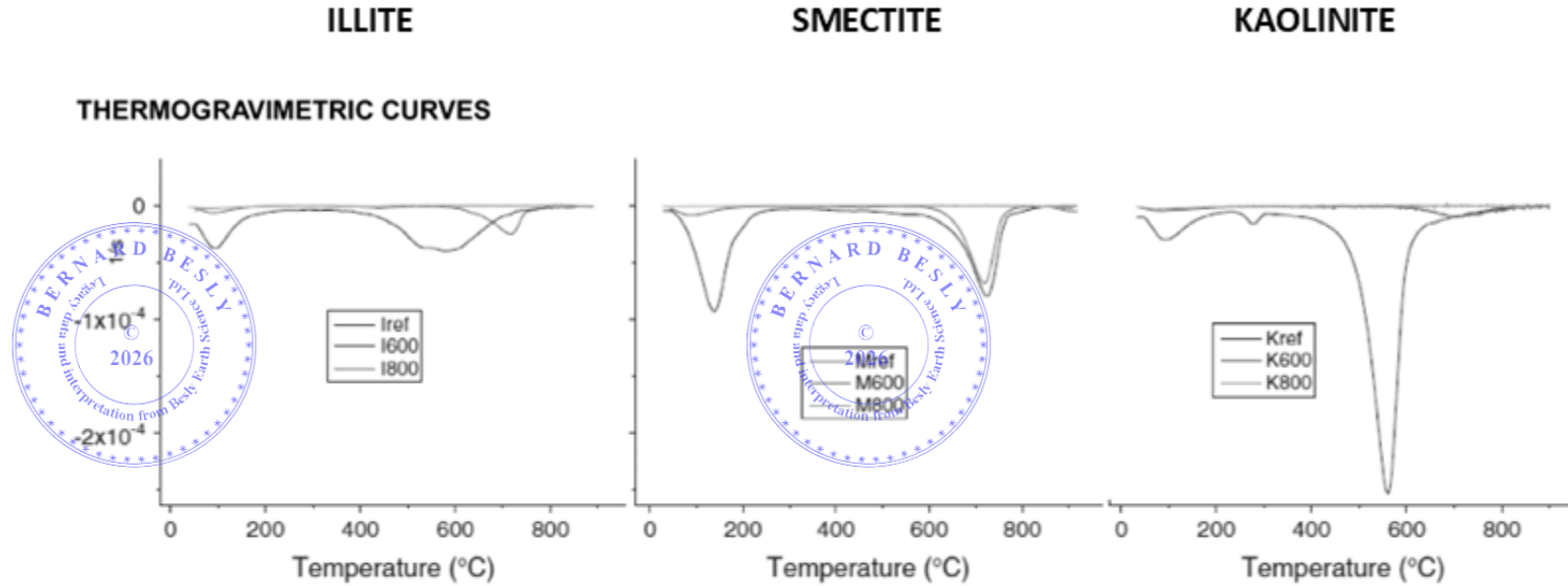
POZZOLANIC CEMENTS & DECARBONISATION

Many routes available to reduce CO₂ emissions in cement making (fuel efficiency, use of biofuels, CCS etc...), but as ±90% of emissions are due to clinker production, substitution of clinker by pozzolans is the most obvious one



Problem: pozzolan sources currently used in developed countries (fly ash, blast furnace slag) are declining in availability

Solution: new pozzolan source found in calcined clays – specifically calcined kaolinitic clays



LC3 CEMENT



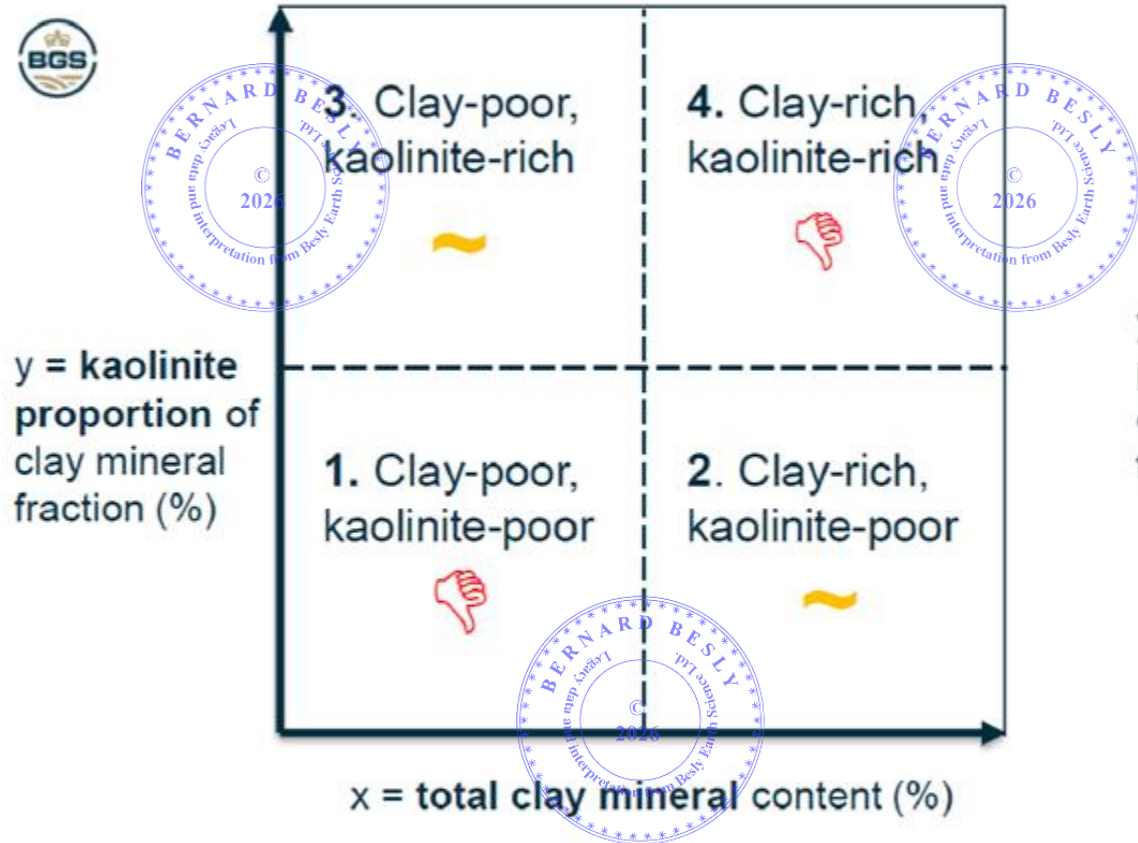
Limestone Calcined Clay Cement ("LC3")

- New cement formulation
- Up to 50% of clinker replaced by calcined clay and limestone
- Estimated 40% emissions savings
 - Lower fuel combustion (clay calcination at $\pm 800^{\circ}\text{C}$, rather than 1400°C)
 - C. 50% less chemical CO_2 from limestone breakdown
- Resulting cement is stronger than OPC and has better corrosion resistance

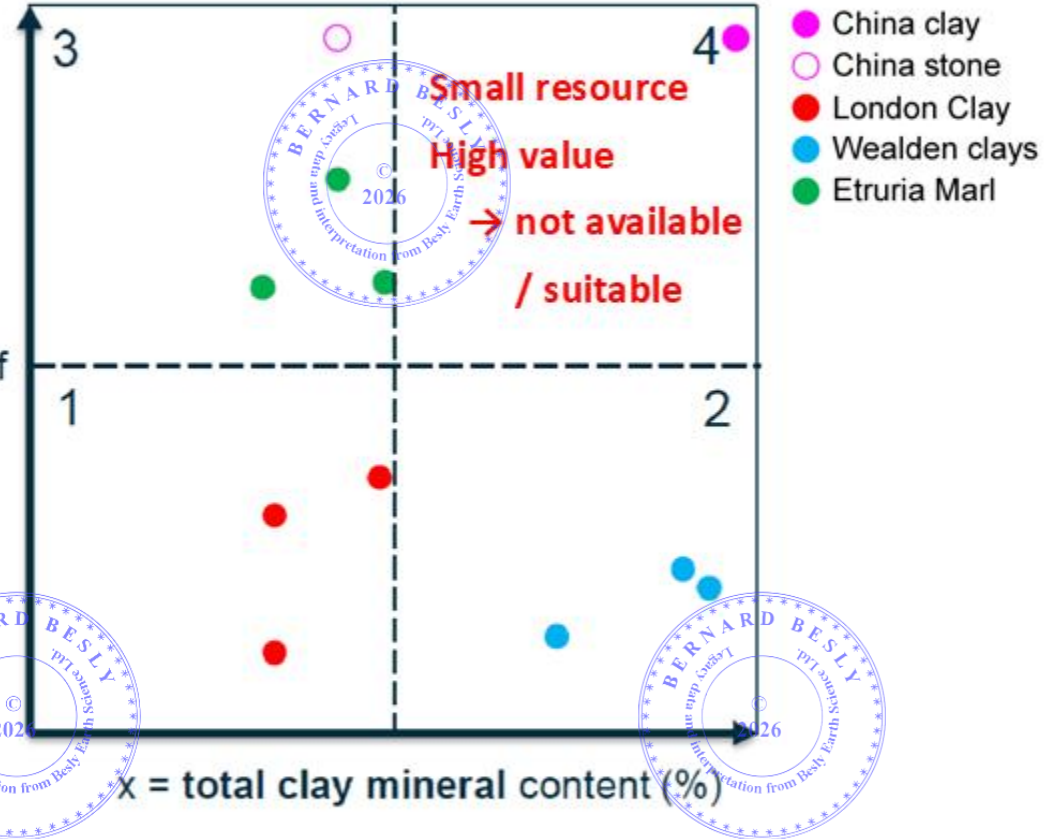
LC3	± 2000	Clinker / calcined clay / limestone / gypsum	$750 - 800^{\circ}\text{C}$	As for hydraulic lime	Y	CSH gel Slow strengthening through CASH gels	CASH gels mop up excess Ca Final strength after 1 year
-----	------------	----------------------------------------------	-----------------------------	-----------------------	---	-------------------------------------------------	-----------------------------------------------------------

Etruria Marl and LC3

CALCINED CLAY FEEDSTOCK SCREENING



y = kaolinite proportion of clay mineral fraction (%)



ETRURIA MARL AS A FEEDSTOCK

Period	Stratigraphy	General clay mineralogy	Basins
Quaternary	Clay-with-flints		
	Estuarine Muds	Smectite, illite, kaolinite	
	Lake Muds		
Tertiary	Till		
	Lough Neagh Beds	Kaolinite (vermiculite, illite)	N Ireland
	Bovey Fm (ball clays)	Kaolinite, (illite, I/S)	Devon
	Solent Gp	Illite, smectite, I/S	S England (Dorset, Hampshire)
	Bracklesham Gp (*ball clays)	Smectite, illite, kaolinite (*), chlorite	
	Thames Gp	Smectite, illite, kaolinite, chlorite	SE & S England
Lower Cretaceous	Lambeth Gp	Smectite, illite, chlorite, kaolinite (*)	
	Lower Greensand Gp	I/S, illite, kaolinite	Wessex, Weald
	Wealden Gp	Kaolinite, illite, I/S	
Jurassic	Cromer Knoll Gp	Illite, I/S	E England
	Kimmeridge Clay Fm	Illite, smectite	S England, Midlands, E & NE England
	Oxford Clay Fm	Smectite, illite	
	Ravenscar Gp	Illite, kaolinite	
	Lias Gp	Illite, kaolinite, berthierine	

Period	Stratigraphy	General clay mineralogy	Basins
Triassic	Mercia Mst Gp	Illite, chlorite, I/S	SW England, Midlands, E England
Permian	Aylesbeare Gp	Kaolinite, illite, I/S	SW England
Pennsylvanian	Salop, Clent Fms	Illite, (kaolinite)	Midlands, N Wales
	Haloscowan Fm		
Mississippian	Etruria Fm	Kaolinite	
	Coal Measures Gp	Kaolinite, illite	
	Millstone Grit Gp	Illite, kaolinite	
Devonian & Palaeozoic	Strathclyde Gp		C & N England, Scotland, S Wales
	Clackmannan Gp	Illite, (I/S)	
	Yoredale Gp		
	Teign Valley Gp	Illite, (I/S)	SW England
	Craven Gp	Illite, (I/S)	C & N England, Scotland, S Wales
		Illite, chlorite	Wales, Welsh borders, SW England, N. England, Midland Valley, Orcadian Basin, Shetland

- Small areas; limited resource
- Existing high-value extractive use
- Mainly environmentally sensitive areas
- In the South.....

- Little known
- Mainly rural, sometimes environmentally sensitive areas

- Established extractive industry
- Known resource
- Etruria more suitable
 - Little CO₂ on calcination
 - CM thin bedded, heterolithic